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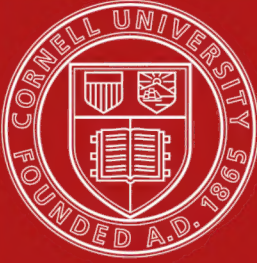
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COLLECTED PAPERS ON
SPECTROSCOPY

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COLLECTED PAPERS ON SPECTROSCOPY

BY

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AND

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IN THE UNIVERSITY OF CAMBRIDGE

WITH A SUPPLEMENTARY PAPER NOT HERETOFORE
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PREFACE

ALL the additions to knowledge which we have contributed in the papers here reprinted have been culled and classified in Kayser's *Handbuch der Spectroscopie*, and it might be thought that no other reproduction was wanted. That was indeed our own view; nevertheless our friends said that the methods and mind of the authors were not told in a record of that sort, and that those now taking up similar research would be really assisted by what they could gather from the detailed account of experiments and *obiter dicta* in the original papers. Moreover the Cambridge University Press offered to undertake almost the whole expense of the re-publication; and the Royal and other learned societies, as well as the Proprietors of the *Philosophical Magazine*, in whose publications our papers first came to light, were willing to allow it. We accepted their offer, and desire to express to these several bodies our hearty thanks.

The papers are reprinted as they originally stood, with only printer's errors corrected. The addition of a diagram for making an obscurity clear is acknowledged. A supplementary paper, not heretofore published, completes the series. We have added a classified index. The papers are records of observations and experiments made each with a definite object in view, but in their course much was noticed which had little direct connection with that object, and was recorded because it bore on other questions of importance or interest in spectroscopy. The bundle of records is consequently very heterogeneous and we hope the index, though the work of an amateur, will help to disentangle it.

G. D. L.

J. D.

Sept. 1915

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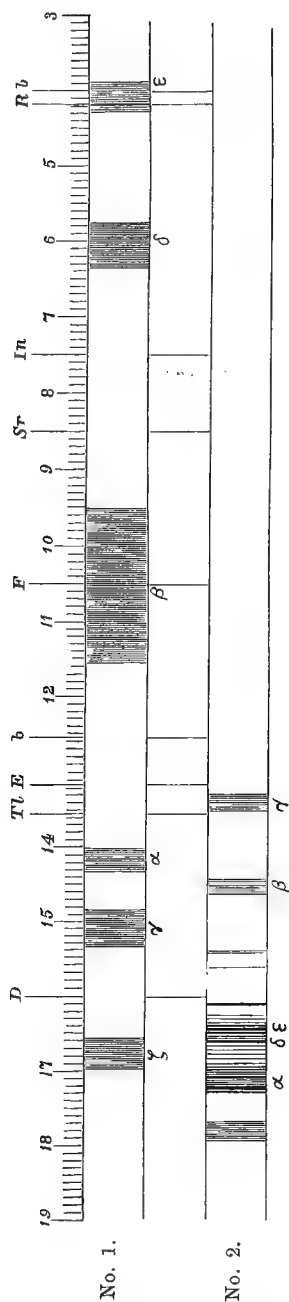
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NOTE ON THE SPECTRA OF CALCIUM FLUORIDE

[*Proceedings of the Cambridge Philosophical Society*,
Vol. III. (1877), p. 96]

No. 1 in the annexed woodcut is the diagram of the spectrum of fluor spar rendered phosphorescent by heat. I have examined several specimens, and all when they begin to be luminous shew a rather narrow band (α) in the green, and a broad band (β) extending into the green and blue about equal distances on either side of Fraunhofer's line F. Common nearly white or pale green fluor does not shew any more bands, but as the temperature rises these two bands widen and nearly meet. Derbyshire bluejohn shews as the temperature rises a second green band (γ) on the yellow side of the first, and then another (ζ) in the orange. The brighter-coloured green fluor, well known for its phosphorescence, shews also at the higher temperature two bands (δ) and (ϵ) in the purple and violet. In every case the bands (α) and (β) appear first and are the most persistent. The light is so faint that it is impossible to see any scale or micrometer distinctly at the same time as the bands, but I have taken the position of the bands of the bright green fluor approximately. The position of the first green band (α) does not appear to be identical in all the specimens, but it is always in the green and on the yellow side of the thallium green line. I have not met with any specimens which shew the spectra described by Kindt in Poggendorf's *Annalen*, cxxxj p. 160; but the spectra described by Becquerel as produced by fluor when exposed to the red rays of the solar spectrum, and attributed by him to the action of heat, agree with the bands I have marked (α) and (β).

No. 2 is the diagram of the spectrum produced by fluor moistened with hydrochloric acid in the flame of a Bunsen's burner: when a solution of fluor in nitric acid is used only the bands marked (α), (β), (γ) and that from (δ) to (ϵ) are seen, the other lines being probably due to the chloride. I have thought it worth while to call attention to this spectrum, because in analysing silicates with the spectroscope it is frequently necessary to decompose them with hydrofluoric acid or alkaline fluorides, and the ordinary text-books do not indicate the existence of the bright green band (γ) which



is very characteristic. Mr Schuster has reminded me that A. Mitscherlich has described the spectrum of calcium fluoride (Pogg. cxxj); but his diagram and description do not give an adequate idea of the spectrum. He makes the band (γ) consist of two about equal and quite distinct parts. It is true that it is divided in two by a fine dark line at about one-third of the breadth of the band from the violet side, but the division is only just visible with such spectroscopes as are ordinarily used for chemical analysis: and it is to be noted that the other green band (β) is divided nearly in the middle by a dark line more easily visible. These dark lines are, however, both too fine to be represented in the woodcut.

ON THE REVERSAL OF THE LINES OF METALLIC VAPOURS

[*Proceedings of the Royal Society*, Vol. XXVII. (1878), pp. 132 sqq.]

SINCE the celebrated paper by Kirchhoff, "On the relation between the radiating and absorbing powers of different bodies for light and heat," in which he detailed the remarkable experiments of reversing the lines of lithium and sodium by sunlight and by the vapours of those metals in the flame of a Bunsen's burner, and mentioned the reversal of the brighter lines of potassium, calcium, strontium and barium when the deflagration of the chlorates with milk-sugar was used instead of the flame of a Bunsen's burner, further researches in the same direction have been made by Cornu, Lockyer, and Roberts. The method adopted by Cornu, which had been previously used by Foucault, is one of great ingenuity, dependent upon so arranging the electric arc that the continuous spectrum of the intensely heated poles is examined through an atmosphere of the metallic vapours volatilized around them. By this means Cornu succeeded in reversing several lines in the spectra of the following metals in addition to those above-mentioned, viz., thallium, lead, silver, aluminium, magnesium, cadmium, zinc, and copper. He observed that in general the reversal began with the least refrangible of a group of lines, and gradually extended to the more refrangible lines of the group; and he drew the conclusion that a very thin layer of vapour was sufficient for the reversal. It may be noted that in almost every case the lines seen by him to be reversed were the more highly refrangible of the lines characteristic of each metal, confirming generally the opinion expressed by Stokes in a letter to Lockyer in the *Proceedings of the Royal Society* for 1876, in which he introduces for the first time the idea of the persistency of different rays with reference to temperature.

The method adopted by Lockyer in the first instance was to view the electric arc through the vapours of the metals volatilized in a stream of hydrogen in a horizontal iron tube.

The iron tube had its ends covered with glass plates, and was heated in a furnace supplied with charcoal. By this means he did not succeed in observing any new reversal of bright lines, but he noticed an unknown absorption line which sometimes appeared when zinc was experimented on. He confirmed, however, the channelled-space absorption spectra observed by

Roscoe and Schuster, in the cases of potassium and sodium, and recorded channelled-space spectra in the case of antimony, phosphorus (?), sulphur (previously observed by Salet) and arsenic (probably). "As the temperature employed for the volatilization of the metals did not exceed bright redness, or that at which cast-iron readily melts, the range of metals examined was necessarily limited; and in order to extend these observations to the less fusible metals, as well as to ascertain whether the spectra of those volatilized at the lower temperature would be modified by the application of a greater degree of heat," a new series of experiments were undertaken by Lockyer and Roberts, in which the combined action of a charcoal furnace and the oxy-hydrogen blowpipe was employed. By this means they obtained no new reversal of a metallic line, but they observed channelled-space spectra in the cases of silver, manganese, chromium, and bismuth. They observed, however, that the metal thallium gave the characteristic *bright green* line, the light of the arc not being reversed.

In the above-mentioned experiments the coolness of the ends of the tube, which acted as condensers of the metallic vapours, and the inequality of density and temperatures necessarily produced by the maintenance of a current of hydrogen in the tube, appear to us to account for the complication and uncertainty of the results of the observations.

In order to examine the reversal of the spectra of metallic vapours, we find it more satisfactory to observe the absorptive effect produced on the continuous spectrum emitted by the sides and end of the tube in which the volatilization takes place. For this purpose we find it convenient to use iron tubes about half-an-inch in internal diameter, and about 27 inches long, closed at one end, thoroughly cleaned inside, and coated on the outside with borax, or with a mixture of plumbago and fireclay. These tubes are inserted in a nearly vertical position in a furnace fed with Welsh coal, which will heat about 10 inches of the tube to about a welding heat, and we observe through the upper open end of the tube, either with, or without, a cover of glass or mica. To exclude oxygen, and avoid as much as possible variations of temperature, we introduce hydrogen in a gentle stream by a narrow tube into the upper part only of the iron tube, so that the hydrogen floats on the surface of the metallic vapour without producing convection currents in it. By varying the length of the small tube conveying the hydrogen, we are able to determine the height in the tube to which the metallic vapour reaches, and to prevent further displacement of the vapour, and thus to maintain different lengths of the iron tube full of metallic vapour at a comparatively constant temperature for considerable periods of time*.

By this means the following observations have been made up to the present time.

* See diagram of apparatus, p. 9.

The first metal experimented on was thallium, one of the most volatile of metals. On inserting some pieces into the hot tube, we had at first great difficulty in avoiding oxidation at the upper surface, and we observed no reversal. However, after arranging the current of hydrogen so as to keep the tube free from air, but without any rapid movement of the gas, we succeeded in seeing the characteristic line reversed, and maintained it so for a considerable time.

The metal indium, closely allied in its behaviour and volatility to thallium, was next examined, and although the amount of this metal at our disposal was not large, we observed the bright blue line reversed. This was most plainly visible when that portion of the vapour which was nearest to the sides of the tube was looked through.

We had great difficulty in preventing the oxidation of magnesium in the tube, and in using tubes wider than half-an-inch did not succeed in getting any reversal, but with half-inch tubes the *b* lines were clearly and sharply reversed, also some dark lines, not measured, were seen in the blue. The sharpness of these lines depended on the regulation of the hydrogen current, by which we could cool the upper stratum of vapour at will.

A piece of metallic lithium was introduced, and gave no results. Sodium was next added in the same tube, and this did not bring out the reversal of the lithium lines. Similarly, chloride of lithium and metallic sodium, introduced together, gave no better results. To a tube containing potassium vapour, some lithium chloride was added, but no lithium line appeared. On adding metallic sodium to this atmosphere, and more lithium chloride, the bright-red lithium line appeared sharply reversed, and remained well defined for a long time. It is worthy of observation that the lithium line was only reversed in a mixture of the vapours of potassium and sodium, and it seems highly probable that a very slightly volatile vapour may be diffused in an atmosphere of a more volatile metal, so as to secure a sufficient depth of vapour to produce a sensible absorption. This would be analogous to well-known actions which take place in the attempt to separate organic bodies of very different boiling points by distillation, where a substance of high boiling point is always carried over, in considerable quantity, with the vapour of a body boiling at a much lower temperature. It is a matter for future investigation how far chemical interactions taking place in a mixture of metallic vapours affect the volatility of a third body, and what relation, if any, this may have to such phenomena as the increased fusibility of mixtures of salts of potassium and sodium, and the well-known fluidity of the alloy of those metals.

As we have had occasion to use sodium and potassium in our tubes, we have had opportunities of observing the absorption spectra of these metals, and we find that there is a great deal yet to be observed in regard to these

spectra. Up to the present time, we have not observed any of the appearances noted by Lockyer, "On a new class of absorption phenomena," in the *Proceedings of the Royal Society*, Vol. xxij, but we have repeatedly noted the channelled-space spectrum of sodium described by Roscoe and Schuster in the same volume of the *Proceedings*. We observed in our tubes no channelled-space absorption by potassium, but continuous absorption in the red, and one narrow absorption band, with a wave-length of about 5730, not corresponding with any bright line of that metal.

With reference to the absorption spectrum of sodium vapour, we may remark that it is by no means so simple as has been generally represented. The fact that the vapour of sodium in a flame shews only the reversal of the D lines, while the vapour, volatilized in tubes, shews a channelled-space absorption corresponding to no known emission spectrum, appears to be part of a gradational variation of the absorption spectrum, which may be induced with perfect regularity. Experiments with sodium, carried out in the way we have described, exhibit the following succession of appearances, as the amount of vapour is gradually diminished, commencing from the appearance when the tube is full of the vapour of sodium, part of it condensing in the cooler portion of the tube, and some being carried out by the slow current of hydrogen. During this stage, although the lower part of the tube is at a white heat, we have always noticed, as long as the cool current of hydrogen displaced metallic vapour, that, on looking down the tube, it appeared perfectly dark. The first appearance of luminosity is of a purple tint, and, with the spectroscope, appears as a faint blue band, commencing with a wave-length of about 4500, and fading away into the violet. Next appears a narrow band in the green, with a maximum of light, with a wave-length of about 5420, diminishing in brightness so rapidly on either side as to appear like a bright line. This green band gradually widens, and is then seen to be divided by a dark band, with a wave-length of about 5510. Red light next appears, and between the red and green light is an enormous extension of the D absorption line, while a still broader dark space intervenes between the green and the blue light. The dark line in the green (wave-length about 5510) now becomes more sharply defined. This line appears to have been observed by Roscoe and Schuster, and regarded by them as coinciding with the double sodium line next in strength to the D lines, but it is considerably more refrangible than that double line. In the next stage, the channelled-space spectrum comes out in the dark space between the green and blue, and finally, in the red. Gradually the light extends, the channels disappear, the D line absorption narrows, but still the dark line in the green is plainly discernible. Lastly, there is only D lines absorption. So far as we can judge, the blue and the streak of green light at first observed are due to luminosity of the vapour itself, where it is somewhat cooled, the later stages being mixed phenomena of absorption and emission.

As the absorption line, with wave-length about 5510, which we may call for shortness the second absorption line of sodium, has not been distinctly recorded by other observers, we have endeavoured to trace it under somewhat different conditions from that of the vapour volatilized in white hot iron tubes. This absorption line is easily seen when a gas flame is observed through a horizontal glass tube, about three inches long, containing sodium volatilized in the middle of the tube by the heat of a Bunsen's burner, and equally well whether the tube contains hydrogen or nitrogen besides sodium. We have also observed the same absorption line when a piece of commercial magnesium ribbon (which always contains sodium) is ignited in a horizontal position, so that the metal melts and produces an elongated flame. It is of some interest to note that absorption lines of about this wave-length, in the solar spectrum, are given by Kirchhoff and Ångström not corresponding with emission lines of known elementary bodies.

When potassium vapour is observed, whether in the iron tube or in a glass tube, an absorption line is seen, with a wave-length of about 5730, which is more refrangible than the yellow double emission line of potassium, and does not correspond to any known bright line of that metal.

We reserve, for a future communication, the discussion of the identity or non-identity of these absorption lines with lines in the solar spectrum and the inferences which may be drawn from such determination.

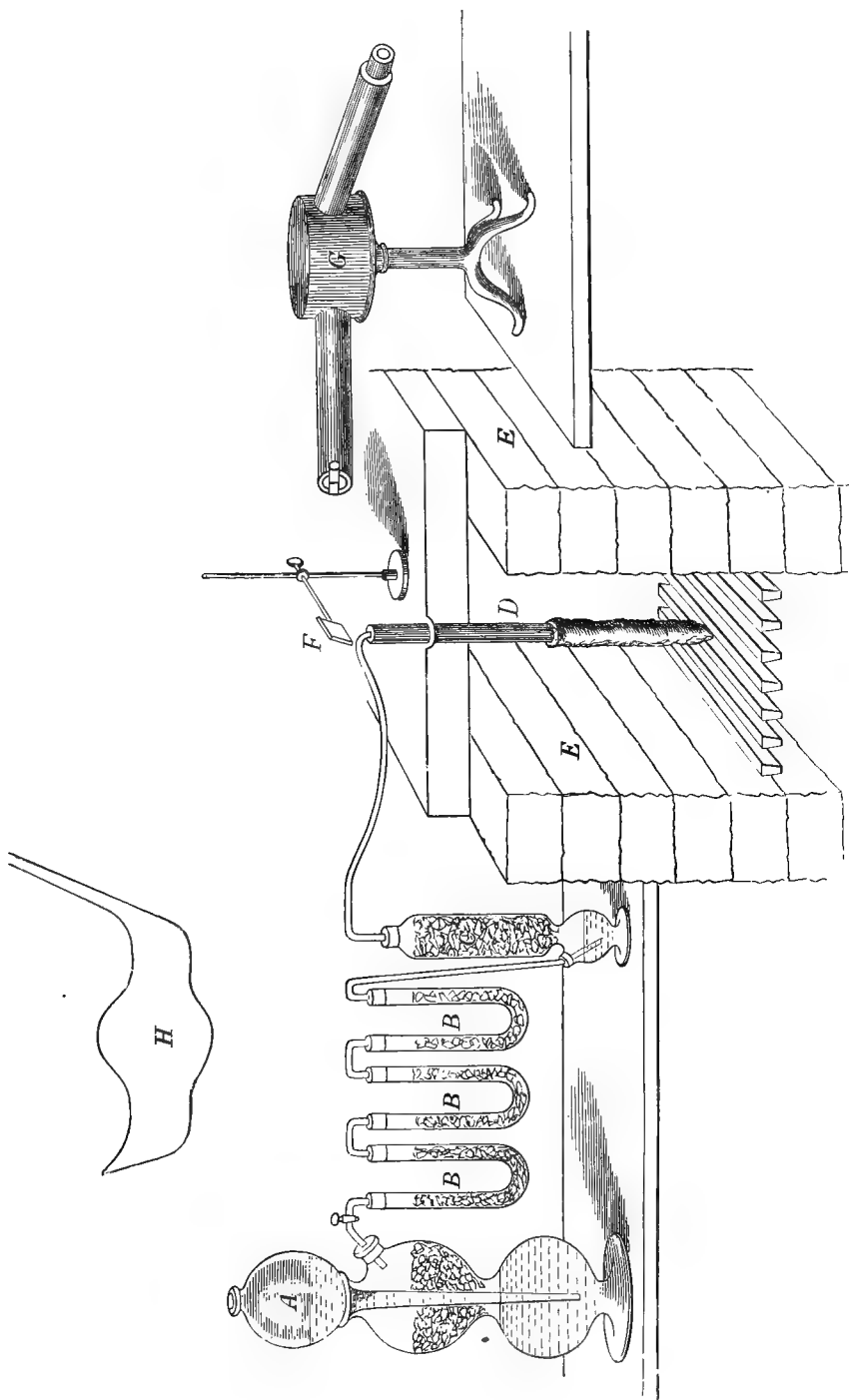
The method of observation we have described may be used to observe emission spectra as well as absorption spectra, for if the closed end of the tube be placed against the bars of the furnace so as to be relatively cooler than the middle of the tube, the light emitted by the vapours in the hottest part is more intense than that emitted by the bottom of the tube. This succeeds admirably with sodium, but we have not specially observed it with other vapours.

ON THE REVERSAL OF THE LINES OF METALLIC VAPOURS

[*Proceedings of the Cambridge Philosophical Society*,
Vol. III. (1878), p. 160]

THE apparatus employed by the authors is represented in the accompanying diagram. *D* is an iron tube half an inch wide and 2 feet long, the lower end closed, and coated with borax or fireclay. This was placed vertically in a small assaying furnace, *E* (shewn in section), 9 inches square and about 12 deep with a good draft, and fed with Welsh coal so that a welding heat was attainable in it. A gentle current of hydrogen from the Kipp's apparatus *A*, purified and dried by passing through the tubes *B* and *C*, was led into *D* by a narrow brass tube reaching to the hot part of *D*. *F* is a small mirror by which the light from the interior of the hot tube was reflected on to the slit of the spectroscope *G*. In the earlier experiments the mirror was omitted, and the spectroscope held above the tube. Fragments of the metals examined were dropped into the tube *D*, and the consequent absorption of the light issuing from the hot bottom of the tube observed with the spectroscope. The most characteristic lines of thallium, indium and magnesium were thus seen directly reversed. The red line of lithium was only seen reversed when potassium, sodium and lithium chloride were all introduced into the tube together.

In the case of sodium besides the D lines they observed a dark line in the green with a wave-length about 5510, and in the case of potassium a dark line with a wave-length about 5730. These lines do not correspond with any known emission lines, though they are in each case near to, but more refrangible than, well-known emission lines of those elements. The channelled spectra described by Roscoe and Schuster (*Proc. R. S.* v 22) were also seen sometimes, but the above-mentioned lines were seen at times when the channelled spectra were not visible. Besides observing potassium and sodium in the iron tubes, they examined the absorption produced by those metals volatilized in glass tubes about 3 inches long, of the form *H* in the accompanying diagram, looking through the length of the tube at a lime light. The ends of these tubes were drawn out so as to present approximately plane faces at the ends, one end being drawn out into a narrow tube by which the



air could be exhausted and other gases introduced at will. In this form of tube the metals could be kept in the state of vapour in the bulb for some time without obscuring the ends. The same absorption lines were seen in the glass tubes as had been observed in the iron tubes. The authors remarked that the density of the vapour of sodium at the temperature of the iron tubes appeared abnormally great, judging from the quantity of the metal which was needed to fill the hot part of the tube with the vapour. As soon as the vapour rose to the level of the end of the small tube conveying the hydrogen, a black cloud of sodium vapour condensed by the cool hydrogen completely obscured all the light from the lower part of the tube, and a smoke of soda issued with the hydrogen from the open end of the tube.

They did not succeed in getting any absorption spectra produced by zinc, cadmium, lead or silver, though all these, except perhaps silver which gave no distinctly recognisable vapour, were volatilized in the tubes.

ON THE REVERSAL OF THE LINES OF METALLIC VAPOURS

[*Proceedings of the Royal Society*, Vol. xxvii. (1878), pp. 350 sqq.]

SINCE our last communication to the Society we have succeeded in reversing characteristic lines of the vapours of rubidium and cæsium. Considering the known volatility of these elements, and the small quantity of their compounds at our disposal, we thought it better to try the effects first in glass tubes. For this purpose a piece of combustion tubing had one end drawn out and the end turned up sharply, and sealed off (like an ill-made combustion tube of the usual form) so as to produce an approximately plane face at the end of the tube; a small bulb was then blown at about an inch from the end, and the tube drawn out at about an inch from the bulb on the other side, so as to form a long narrower tube*. Some dry rubidium or cæsium chloride was next introduced into the bulb, and a fragment of fresh cut sodium, and the narrow part of the tube turned up, so as to allow the tube and bulb to be seen through in the direction of the axis of the tube. The open end was then attached to a Sprengel pump, and the air exhausted; the sodium was then melted, and afterwards either dry hydrogen or dry nitrogen admitted, and the end of the tube sealed off at nearly the atmospheric pressure. We found it necessary to have this pressure of gas inside the tube, otherwise the metal distilled so fast on heating it that the ends were speedily obscured by condensed drops of metal. Through these tubes placed lengthways in front of a spectroscope, a lime light was viewed. On warming the bulb of a tube in which rubidium chloride had been sealed up with sodium, the D lines were of course very soon seen, and very soon there appeared two dark lines near the extremity of the violet light, which, on measurement, were found to be identical in position with the well-known violet lines of rubidium. Next appeared faintly the channelled spectrum of sodium in the green, and then a dark line in the blue, very sharp and decided, in the place of the more refrangible of the characteristic lines of cæsium in the flame spectrum. As the temperature rose these dark lines, especially those in the violet, became sensibly broader; and then another fine dark line appeared in the blue, in the place of the less refrangible of the cæsium blue lines. During

* See diagram of apparatus in connexion with the preceding paper.

this time no dark line could be observed in the red, but as the temperature rose a broad absorption band appeared in the red, with its centre about midway between B and C, ill-defined at the edges, and though plainly visible not very dark. The lines in the violet had now become so broad as to touch each other and form one dark band. On cooling, the absorption band in the red became gradually lighter without becoming defined, and was finally overpowered by the channelled spectrum of sodium in that region. The double dark line in the violet became sharply defined again as the temperature fell. There are two blue lines in the spectrum of rubidium taken with an induction-coil very near the two blue lines of caesium, but they are comparatively feeble, and the two dark lines in the blue which we observed in the places of the characteristic blue lines of caesium we believe must have been due to a small quantity of caesium chloride in the sample of rubidium chloride. These blue lines were not, however, visible when some of the rubidium chloride was held in the flame of a Bunsen's burner, nor when a spark was taken from a solution of the chloride; but the more refrangible of them ($Cs\alpha$) was visible in the spark of an induction-coil, without a Leyden jar, taken between beads of the rubidium chloride fused on platinum wires.

When a tube containing caesium chloride and sodium was observed, in the same way as the former, the two dark lines in the blue were seen very soon after the heating began, and the more refrangible of them broadened out very sensibly as the temperature increased. The usual channelled spectrum of sodium was seen in the green, and an additional channelling appeared in the yellow, which may be due to caesium or to the mixture of the two metals. We have at present no metallic caesium wherewith to decide this question. Indeed the caesium chloride used was not free from rubidium, and the dark lines of rubidium were distinctly seen in the violet.

It is remarkable that these absorption lines of caesium coincide with the blue lines of caesium as seen in the flame, not with the green line which that metal shews when heated in an electric spark of high density. It is to be observed, however, that when sparks from an induction-coil without a jar are taken between beads of caesium chloride, fused on platinum wires, a spectrum similar to the flame spectrum is seen, and it is only when a Leyden jar is used that the spectrum is reduced to a green line. In like manner both the violet lines of rubidium are reversed in our tubes, and both these violet lines are seen when the spark of an induction-coil, without jar, is passed between beads of rubidium chloride fused on platinum wire, though only one of them appears when a Leyden jar is used.

We have not repeated these observations on caesium and rubidium in iron tubes, because the light emitted from the hot iron does not extend so far into the violet as the rubidium lines, and the amount of caesium at our command at present is very small.

We have extended our observations on the absorption of magnesium and of mixtures of magnesium with potassium and sodium, using iron tubes placed vertically in a small furnace fed with Welsh coal, as described in our former communication.

The result of several observations, when commercial magnesium (*i.e.*, magnesium with only a small percentage of sodium in it) was used, is that the absorption produced by magnesium consists of—

(1) Two sharp lines in the green, of which one, which is broader than the other, and appears to broaden as the temperature increases, coincides in position with the least refrangible of the *b* group, while the other is less refrangible, and has a wave-length very nearly 5210. These lines are the first and the last to be seen and very constant, and we at first took them for the extreme lines of the *b* group*

(2) A dark line in the blue, always more or less broad, difficult to measure exactly, but very near the place of the brightest blue line of magnesium. This line was not always visible, indeed rarely when magnesium alone was placed in the tube. It was better seen when a small quantity of potassium was added. The measure of the less refrangible edge of this band then gave a wave-length of very nearly 4615. It was also seen when sodium and magnesium were used together, but it was more difficult to get a measure of it in this case, as the sodium obscures the blue part of the spectrum. A measure taken when sodium was used gave a wave-length 4580, but this can only be regarded as an approximation.

(3) A third line or band in the green rather more refrangible than the *b* group. This is best seen when potassium as well as magnesium is introduced into the tube, but it may also be seen with sodium and magnesium. The less refrangible edge of this band is sharply defined, and has a wave-length about 5140, and it fades away towards the blue.

These absorptions are all seen both when potassium and when sodium are used along with magnesium, and may be fairly ascribed to magnesium, or to magnesium together with hydrogen.

But besides these, other absorptions are seen which appear to be due to mixed vapours.

(4) When sodium and magnesium are used together a dark line, with ill-defined edges, is seen in the green, with a wave-length about 5300. This is the characteristic absorption of the mixed vapours of sodium and magnesium, it is not seen with either vapour separately, nor is it seen when potassium is used instead of sodium.

(5) When potassium and magnesium are used together, a pair of dark lines are seen in the red. The less refrangible of these sometimes broadens

* On one occasion a dark line corresponding to b_2 was also seen.

into a band with ill-defined edges, and has a mean wave-length of about 6580. The other is always a fine sharp line, with a wave-length about 6475. These lines are as regularly seen with the mixture of potassium and magnesium as the above-mentioned line (5300) is seen with the mixture of sodium and magnesium, but are not seen except with that mixture.

(6) On one occasion, with a mixture of potassium and magnesium, another dark line was seen in the blue, with a wave-length nearly 4820. This line is very near one of the bright lines, seen when sparks from an induction-coil, without a Leyden jar, are taken between electrodes of magnesium, and may very likely be due to magnesium alone, and not to the mixture of vapours, as we only observed it on one occasion.

There is a certain resemblance between the absorptions above ascribed to magnesium, and the emission spectrum seen when the sparks of a small induction-coil, without Leyden jar, are taken between electrodes of magnesium. This emission spectrum is the same, with the addition of some blue lines, as that seen when the sparks are taken from a solution of magnesium chloride, as accurately described by Lecoq de Boisbaudran (*Spectres lumineux*, p. 86), and as that seen in burning magnesium (Dr W. M. Watts, *Phil. Mag.*, 1875), and consists, as we have observed, of lines with the following wave-lengths:—4481, 4590 (Thalén 4586), 4570 (Thalén 4565), 4797, 4930, 4945, 4957, 4969, 4980, 4990, 5000, the well-known *b* group, and 5528 (Thalén).

The pair of lines (1) correspond nearly with the *b* group, but slightly displaced towards the red; the shaded band (3) corresponds less closely to the series of seven lines 5000 to 4930, which progressively decrease in brightness towards the blue, and is also a little less refrangible than that series; the broad line in the blue (2) corresponds to the pair of lines 4570 and 4590, and the remaining line (6) with the line 4797, also both displaced a little towards the red. No absorption corresponding to the extreme lines 4481 and 5528 was observed. There is plainly no exact reversal except of the line b_1 , and even in that case it may be an accident if we suppose the two dark lines (1) to represent the extreme line of the group *b*. It may be noted in connexion with this that the absorption lines described by us in our former communication as seen with sodium and potassium (wave-lengths 5510 and 5730) are near to, but *more* refrangible than, well-known emission lines of those elements.

The absorptions produced by the mixtures of vapours plainly offer a wide field for further observation. At present we have not succeeded in observing those produced by mixtures of vapours other than those here recorded; and it seems needful to use tubes of a less fusible material than iron, which, notwithstanding the protection of fireclay, very quickly gives way at the temperatures we have used.

With regard to those above described, we may observe that there is in the solar spectrum an absorption line, hitherto unaccounted for, closely corresponding to each of them. Thus, on Ångström and Thalén's map there are dark lines at 6580 and 6585, with more or less continuous absorption between them, a broad dark line between 6474 and 6475, and a dark line at 5300. There are also dark lines nearly, if not exactly, coincident with the series of seven bright lines of magnesium above described, which we have not seen strictly reversed. The coincidences of the series of the solar spectrum hitherto observed have, for the most part, been with lines given by dense electric sparks; while it is not improbable that the conditions of temperature, and the admixtures of vapours in the upper part of the solar atmosphere, may resemble much more nearly those in our tubes.

We intend to pursue our observations, using higher temperatures, if we can obtain tubes which will stand under those circumstances.

ON THE REVERSAL OF THE LINES OF METALLIC VAPOURS

[*Proceedings of the Royal Society*, Vol. xxvii. (1878), pp. 494 sqq.]

IN our last communication to the Royal Society we described certain absorption lines, which we had observed to be produced by the vapour of magnesium in the presence of hydrogen, and certain other lines which were observed when potassium, and others when sodium, was present, in addition to magnesium and hydrogen. These lines correspond to no known emission lines of those elements; but, inasmuch as they appeared to be regularly produced by the mixtures described, and not otherwise, we could only ascribe their origin to the mixtures as distinct from the separate elements. It became a question of interest, then, whether we could find the conditions under which the same mixtures would give luminous spectra, consisting of the lines which we had seen reversed. On observing sparks from an induction-coil taken between magnesium points in an atmosphere of hydrogen, we soon found that a bright line regularly appeared, with a wave-length about 5210, in the same position as one of the most conspicuous of the dark lines we had observed to be produced by vapour of magnesium with hydrogen in our iron tubes. This line is best seen, *i.e.* is most steady, when no Leyden jar is used, and the rheotome (the coil we used has an ordinary self-acting one) is screwed back, so that it will but just work. It may, however, be seen when the coil is in its ordinary state, and when a small Leyden jar is interposed; but it disappears (except in flashes) when a larger Leyden jar is used, if the hydrogen be at the atmospheric pressure. This line does not usually extend across the whole interval between the electrodes, and is sometimes only seen near the negative electrode. Its presence seems to depend on the temperature, as it is not seen continuously when a large Leyden jar is employed, until the pressure of the hydrogen and its resistance is very much reduced. When well dried nitrogen or carbonic oxide is substituted for hydrogen, this line disappears entirely; but if any hydrogen or traces of moisture be present it comes out when the pressure is much reduced. In such cases the hydrogen lines C and F are always visible as well. Sometimes several fine lines appear on the more refrangible side of this line, between it and the *b* group, which give it the appearance of being a narrow band,

shaded on that side. We have used various samples of magnesium as electrodes, and they all give the same results. We have also used hydrogen prepared and purified in different ways: hydrogen prepared by the action of zinc on dilute sulphuric acid, purified by an acid solution of bichromate or permanganate, and by potash, and dried by sulphuric acid; electrolytic hydrogen; hydrogen from dry formate of soda and soda lime; hydrogen occluded by sodium and expelled by heat; and hydrogen occluded by palladium and expelled by heat. In the last two cases the whole apparatus was connected by fusion, and a Sprengel pump, also connected by fusion, employed to remove the air. In all cases the phenomena were the same.

In addition to the above-mentioned line, we observed that there is also produced a series of fine lines, commencing close to the most refrangible line of the *b* group, and extending with gradually diminishing intensity towards the blue. These lines are so close to one another, that in a small spectroscope they appear like a broad shaded band. We have little doubt that the dark absorption line, with wave-length about 5140, shading towards the blue, which we previously observed in our iron tubes, and described in our last communication, was a reversal of part of these lines, though the latter extend much further towards the blue than we had observed the absorption to extend. In fact, the bright lines extend somewhat more than half the distance between *b* and *F*, from 45 to 50 being visible, and placed at nearly equal distances from each other. They also commence close to the *b* group, *i.e.* with a wave-length nearly 5164, but the first two or three lines at that end are not so bright as those which immediately succeed them. The light giving these lines does not extend to more than a short distance from the electrodes, and is generally most conspicuous at the negative electrode. There is a difficulty in consequence of the flickering character of the discharge in getting any accurate measures of them, though they are bright enough, especially at the less refrangible end, to be easily seen. The comparative faintness of the light from the iron tubes appears to us almost sufficient to account for our not having seen the reversed lines so completely as the bright ones; nevertheless, it is quite in accordance with what we in other cases observed, to suppose that some of these lines may be more easily reversed at the temperature of the iron tubes than others.

STUDIES IN SPECTRUM ANALYSIS

[*Proceedings of the Cambridge Philosophical Society*, Vol. III.
(1878), p. 208]

THE authors describe the reversal of characteristic lines of rubidium and cæsium when the chlorides are heated with sodium in glass tubes in an atmosphere of hydrogen or nitrogen, and a bright light is viewed through the vapours. They remark that the violet lines of rubidium, and the most refrangible of the cæsium lines are first seen, and when the temperature rises broaden out the most, contrary to what might have been expected from the analogy of other cases. The absorption lines observed coincided with the bright lines of the metals heated in a flame, not with the lines which they give in a dense electric spark; but the authors obtained spectra similar to the flame spectra by passing sparks from an induction coil, without a Leyden jar, between beads of fused chlorides of those metals, although simpler spectra were produced by the more abrupt discharges produced by interposing a Leyden jar. The authors further described absorption spectra produced by magnesium vapour when mixed with hydrogen, potassium, and sodium respectively. That produced by magnesium and hydrogen consisted of a line a little less refrangible than the *b* group, and a band rather more refrangible than the *b* group, fading away towards the blue. The constant appearance of these absorptions when the vapour of magnesium in hydrogen was observed in a hot iron tube, led to the endeavour to obtain the corresponding luminous spectrum. This they succeeded in doing by taking sparks from an induction coil, without a Leyden jar, between magnesium wires in a tube full of hydrogen. It appears that the compound to which this spectrum is due is formed only within a certain range of temperature, and is dissociated at higher temperatures—for the spectrum is scarcely seen at all when a large Leyden jar is used, which may be supposed to have the effect of shortening the time of discharge and increasing the temperature. Further, this compound does not seem to be formed when the pressure of the hydrogen is much reduced. In the case of sodium and magnesium they observed an absorption line in the green not observed in either vapour separately; and when potassium and magnesium were used, a characteristic pair of lines in the red always appeared, and sometimes another line in the blue. The authors have

not yet seen these as bright lines. In the course of observations on the spectra of sundry rarified gases the authors have been led to conclude that electric sparks take a selective course in a mixture of gases, and that the differences in the spectra observed in different parts of the same tube are probably due to the existence of more than one gas in the tube. Tubes of nitrogen which did not shew the lines of hydrogen at all when sparks from an induction-coil without a Leyden jar were passed through them, gave strong hydrogen lines when a large jar was interposed. A bulb tube with magnesium wires filled with hydrogen at low pressure gave in one half scarcely any spectrum but the F line of hydrogen, while the other half gave the spectrum of acetylene. They generally found hydrogen lines, and flashes of sodium (no doubt from the glass) in tubes very much exhausted; and they conclude that impurities enter such tubes from sources hitherto unsuspected. Tubes filled with oxygen obtained from silver iodate have been found to give the spectrum of iodine, pointing to the conclusion that chemical reactions occur at very low pressures which are not produced under other circumstances. Generally the authors conclude that the spectrum of a gas in a rarefied state affords the most delicate test of its purity, and that it is to the chemical problem of obtaining pure gases that attention needs to be specially directed.

ON THE REVERSAL OF THE LINES OF METALLIC VAPOURS

[*Proceedings of the Royal Society*, Vol. xxviii. (1879), p. 352]

IN the experiments described in the following communication, instead of introducing the substances to be observed in the metallic form into our tubes, we have endeavoured to overcome, to some extent, the difficulty of the presence of impurities by making use of reactions which should generate the metallic vapours within the tubes. For this purpose we have generally employed the great reducing power of carbon and of aluminium at high temperatures.

In a former communication (*Proc. Roy. Soc.*, Vol. xxvii p. 350) we described the reversal of the two blue lines of cæsium and the two violet lines of rubidium by the vapours of those metals, produced by heating their chlorides with sodium in glass tubes. It might be doubtful from these experiments whether the absorption were due to the metals or to the chlorides. To decide this question, we first tried cæsium chloride by itself, heated in a tube such as we used before. No absorption lines could be seen, although a good deal of the chloride had been vaporized and distilled to the cool part of the tube. The experiments were next repeated, both with rubidium and cæsium chlorides along with metallic lithium. The two violet lines of rubidium and the two blue lines of cæsium were reversed, as when sodium was used instead of lithium, and as the lithium gave no sensible vapour, the observations could easily be continued for a much longer time with the same tubes. No other absorption lines could be discerned. It may be observed, however, that it is not easy to obtain a source of light sufficiently rich in the least refrangible red to allow of observations on the absorption of light so little refrangible as the red rubidium lines. A platinum wire, heated nearly to fusion by an electric current, appeared to give the brightest light in this part of the spectrum, but of that light no definite absorption by the rubidium could be observed in the red. We then had some mixtures of carbonate of cæsium with carbon, and of carbonate of rubidium with carbon, prepared by charring the tartrates; and observed the results of heating these mixtures in narrow porcelain tubes, placed vertically in a furnace, as described in our first communication on this subject (*Proc. Roy. Soc.*, Vol. xxvii). A small quantity of the cæsium mixture, introduced into a tube at a bright red heat, shewed

instantly the two blue lines reversed, and so much expanded as to be almost in contact. The width of the dark lines decreased as the *cæsium* evaporated, but they remained quite distinct for a very long time. A similar effect was produced by the rubidium mixture, only it was necessary to have the tube very much hotter, in order to get enough of violet light to see the reversal of the rubidium lines. In this case the two lines were so much expanded as to form one broad dark band, which gradually resolved itself into two as the rubidium evaporated. The reversal of these lines of *cæsium* and rubidium seems to take place almost or quite as readily as that of the D lines by sodium, and the vapours of those metals must be extremely opaque to the light of the refrangibility absorbed, for the absorption was conspicuous when only very minute quantities of the metals were present. The red, yellow, and green parts of the spectrum were carefully searched for absorption lines, but none due to *cæsium* or rubidium could be detected in any case. It is perhaps worthy of remark that the liberation of such extremely electro-positive elements as *cæsium* and rubidium from their chlorides by sodium and by lithium, though it is probably only partial, is a proof, if proof were wanting, that so-called chemical affinity only takes a part in determining the grouping of the elements in such mixtures; and it is probable that the equilibrium arrived at in any such case is a dynamical or mobile equilibrium, continually varying with change of temperature.

Our next experiments were with charred cream of tartar in iron tubes, arranged as before. In this case a broad absorption band appeared, extending over the space from about wave-length 5700 to 5775, and in some cases still wider, with edges ill-defined, especially the more refrangible edge. By placing the charred cream of tartar in the tube before it was introduced into the furnace, and watching the increase of light as the tube got hot, this band was at first seen bright on a less bright background, it gradually faded, and then came out again reversed, and remained so. No very high temperature was required for this, but a rise of temperature had the effect of widening the band. Besides this absorption, there appeared a very indefinite faint absorption in the red, with the centre at a wave-length of about 6100, and a dark band, with a tolerably well-defined edge on the less refrangible side, at about a wave-length of 4850, shading away towards the violet. A fainter dark band was sometimes seen beyond, with a wave-length of about 4645; but sometimes the light seemed abruptly terminated at about wave-length 4850. It will be noticed that these absorptions are not the same as those seen when potassium is heated in hydrogen, nor do they correspond with known emission lines of potassium, although the first, which is also the most conspicuous and regularly visible of these absorptions, is very near a group of three bright lines of potassium. It seemed probable that they might be due to a combination of potassium with carbonic oxide. We tried the effect of heating potassium in carbonic oxide in glass tubes, but, though the potassium

united readily with the gas, the compound did not appear to volatilize at a dull red heat, and no absorption, not even that which potassium gives when heated in nitrogen under similar circumstances, could be seen. We then tried induction sparks between an electrode of potassium and one of platinum in an atmosphere of carbonic oxide. The usual bright lines of potassium were seen, and also a bright band, identical in position with the above-mentioned band, between wave-lengths about 5700 and 5775. This band could not be seen when hydrogen was substituted for carbonic oxide. A mixture of sodium carbonate and charred sugar, heated in an iron tube, gave only the same absorption as sodium in hydrogen. There were also no indications of any absorption due to a compound of rubidium or of cæsium with carbonic oxide.

The experiments of Mallet (*Chem. Soc. J.*, 1876) on the volatility of calcium, strontium, and barium, and the reducing action of aluminium on the oxides, especially in the presence of carbonate of sodium, induced us to try similar mixtures in our tubes.

A mixture of barium carbonate, aluminium filings, and lamp-black, heated in a porcelain tube, gave two absorption lines in the green, corresponding in position to bright lines seen when sparks are taken from a solution of barium chloride, at wave-lengths 5242 and 5136, marked α and β by Lecoq de Boisbaudran. These two absorptions were very persistent, and were produced on several occasions. A third absorption line, corresponding to line δ of Boisbaudran, was sometimes seen, and on one occasion, when the temperature was as high as could be obtained in the furnace fed with Welsh coal, and a mixture of charred barium tartrate with aluminium was used, a fourth dark line was seen with wave-length 5535. This line was very fine and sharply defined, whereas the other three lines were ill-defined at the edges; it is, moreover, the only one of the four which corresponds to a bright line of metallic barium.

Repeated experiments with charred tartrates of calcium and of strontium mixed with aluminium gave no results, but on one occasion, when some sodium carbonate was used along with the charred tartrate of strontium and aluminium, the blue line of strontium was seen reversed, and on another occasion, when a mixture of charred potassium, calcium, and strontium tartrates, and aluminium was used, the calcium line, with wave-length 4226, was seen reversed. The fire in this case was fed with gas retort carbon, and the temperature such that iron tubes, though well coated with fire-clay, gave way in a few minutes. It appears, therefore, that the blue line of strontium, and the above-mentioned violet line of calcium, are reversible by this method, but not so easily or so certainly as the lines of barium or its compounds above mentioned.

In order to obtain higher temperatures than we could obtain in the furnace used in our former experiments, we have made preliminary experiments

with lime crucibles heated (1) by a jet of coal-gas and oxygen; (2) by the electric arc. For this purpose a block of chalk or lime has a vertical tubular hole bored into it about 6 or 7 millims. in diameter, and for the gas jet a second lateral boring, meeting the other boring at the bottom (fig. 1). For the electric arc two lateral borings are made on opposite sides of the block, meeting the vertical boring at its bottom (fig. 2). Above the crucible we place a mirror inclined at 45° , so as to reflect the light from the vertical boring on to the slit of a spectroscope, a plate of mica being interposed between the mirror and crucible to deflect the stream of hot gas and catch the smoke, which would otherwise soon dim the surface of the mirror.

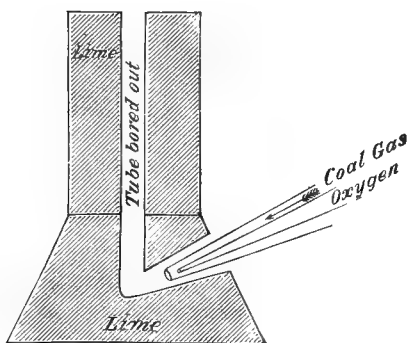


FIG. 1.

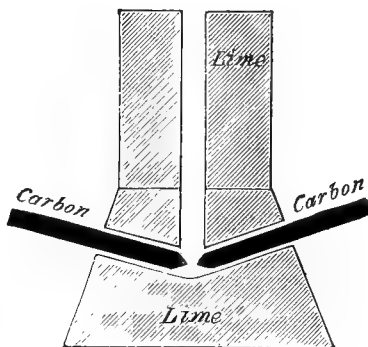


FIG. 2.

With the jet of coal-gas and oxygen the usual green and orange bands of lime and the violet line of calcium (wave-length 4226) were seen bright on the continuous spectrum, and on dropping in some aluminium their brightness increased at the same time that a dark line appeared in the middle of both the orange and green band. This dark line speedily disappeared in the case of the orange band, but lasted longer in the green band. When some lithium carbonate was put into the crucible and the coal-gas turned on so as to be in excess, the red lithium line was reversed, appearing slightly expanded with a black line down the middle.

For the electric arc 25 Grove's cells were used, and the carbon poles introduced through the lateral openings, so as to meet at the bottom of the vertical boring of the lime crucible. A very brilliant spectrum of bright lines was produced on bringing the poles in contact, while a copious stream of vapours ascended the tube. On drawing apart the poles, which could be done

for nearly an inch without stopping the current, the calcium line (wave-length 4226) was seen reversed. On dropping some aluminium into the crucible the calcium line just mentioned was very much expanded, and appeared with a broad black line in the middle. The other calcium lines in the neighbourhood on the less refrangible side were also expanded considerably, but were not seen reversed. The more refrangible lines (Fraunhofer's H), however, remained sharply defined, and did not appear sensibly expanded or reversed.

On introducing some strontia the blue strontium line (wave-length 4607) was immediately seen reversed, appearing as a broadish bright band, with a dark line in the middle. There were no indications of the reversal of any other strontium line, though the more refrangible lines were conspicuously bright.

When lithium carbonate was introduced the red line was at once seen reversed, but not much expanded. When some aluminium was added, the lithium blue line (wave-length 4604) was seen with a dark line in the middle for a short time only. The green line of lithium was very bright indeed, and appeared somewhat expanded on the addition of aluminium, but shewed no reversal.

On putting some baryta into the crucible the line with wave-length 5535 was reversed, appearing very black but narrow. No other barium line could be seen reversed in that crucible, but in another crucible into which magnesia had been introduced, a dark line, with wave-length about 4930, was observed, which may probably be ascribed to barium.

With magnesia and aluminium the least refrangible of the *b* group was seen reversed, all the *b* group being expanded.

When silver was introduced, on drawing the poles apart, both the brightest green lines (wave-lengths 5464 and 5209) were seen for a short time with a black line down the middle.

Frequently on parting the poles, whatever might be the substance in the crucible, the whole of the brightest part of the spectrum, from the orange to the blue, appeared filled with dark lines, all equidistant and equally dark, like a fine grating. With a high dispersion these lines are seen to be ill-defined at the edges. We can only suppose them to be a banded spectrum of some compound of carbon.

The lime crucibles are very quickly destroyed, but we hope to get some more compact lime than we have hitherto had, and to employ a more powerful electric current. The use of carbon or magnesia for crucibles will, we anticipate, enable experiments of this kind to be extended much further, and applied to various reactions taking place at the temperature of the arc.

In the case of carbon crucibles the block of carbon itself will form one electrode, the other electrode passing through a tube of lime as in fig. 3. It is our intention to try a combination of the electric arc and induction spark in these crucibles. It is hardly necessary to note that the projection of the reversals of the lines of metallic vapours may be effected by this method better than by any method heretofore in use.

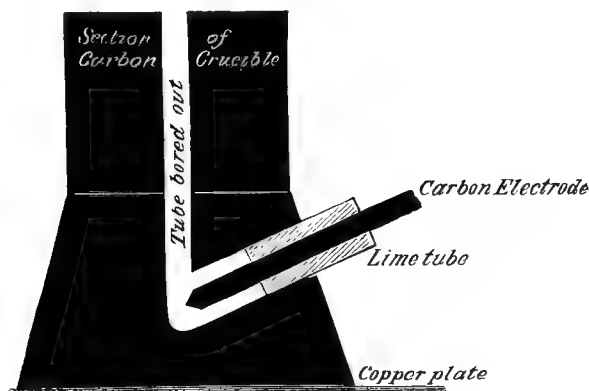


FIG. 3.

ON THE REVERSAL OF THE LINES OF METALLIC VAPOURS

[*Proceedings of the Royal Society*, Vol. XXVIII. (1879), p. 367]

SINCE our last communication we have continued our experiments, using the electric arc as a source of heat, in lime and in carbon crucibles as described before. Success depends on getting a good stream of vapour in the tubular part of the crucible. This is easily attained in the lime crucibles, which quickly reach a very high temperature, but are very soon destroyed; not so certainly in the carbon crucibles, which are good conductors of heat. The latter, however, last for a very long time.

In our experiments with tubes heated in a furnace we used a small spectroscope with a single prism, which gave a good definition and plenty of light; but in the experiments here described we have used a larger spectroscope by Browning, with two prisms of 60° and one of 45° , taking readings on a graduated circle instead of on a reflected scale.

Both in the lime and in the carbon crucibles we have found that the finely channelled spectrum, extending with great uniformity from end to end, always made its appearance so long as the poles were close together. A few groups of bright lines appear on it. We have not at present investigated this remarkable spectrum further. In several cases we have observed the absorption lines of the metals put into the crucibles on this channelled spectrum as a background, but generally when the vapours in the crucibles become considerable, the channellings give place to a spectrum of bright lines on a much less bright continuous background; we have used generally thirty cells in the galvanic battery, sometimes only twenty-five, once forty.

The calcium line with wave-length 4226 almost always appears more or less expanded with a dark line in the middle, both in the lime crucibles and in carbon crucibles into which some lime has been introduced; the remaining bright lines of calcium are also frequently seen in the like condition, but sometimes the dark line appears in the middle of K (the more refrangible of Fraunhofer's lines H), when there is none in the middle of H. On throwing some aluminium filings into the crucible, the line 4226 appears as a broad dark band, and both H and K as well as the two aluminium lines between them appear for a second as dark bands on a continuous background. Soon

they appear as bright bands with dark middles; gradually the dark line disappears from H, and afterwards from K, while the aluminium lines remain with dark middles for a long time. When a mixture of lime and potassium carbonate (to produce a stronger current of vapour in the tube) was introduced into a carbon crucible the calcium (?) line with wave-length 4095 was seen strongly reversed, and the group of three lines with wave-lengths 4425, 4434, and 4454 were all reversed, the least refrangible being the most strongly reversed, and remaining so the longest, while the most refrangible was least strongly reversed and for the shortest time.

Besides these reversals, which were regularly observed, the following were noticed by us as occurring in lime crucibles but with less certainty, perhaps only at the highest temperatures. Dark bands appearing for a short time and dwindling into sharp dark lines with wave-lengths about 6040 and 6068 (perhaps due to the oxide); a dark line replacing the most refrangible of a well-marked group of several bright lines with wave-length 5581 (or possibly the brighter line 5588); and the lines with wave-lengths 6121 and 6161 reversed simultaneously for an instant and reappearing bright immediately; and the line with wave-length 5188 reversed. When aluminium was put into the crucible only the two lines of that metal between H and K were seen reversed. The lines at the red end remained steadily bright.

When some magnesium was put into a lime crucible, the *b* group expanded a little without appearing reversed, but when some aluminium was added, the least refrangible of the three lines appeared with a dark middle, and on adding more magnesium the second line put on the same appearance; and lastly, the most refrangible was reversed in like manner. The least refrangible of the three remained reversed for some time; and the order of reversibility of the group is the inverse of that of refrangibility. Of the other magnesium lines, that in the yellowish-green (wave-length 5527) was much expanded, the blue line (wave-length 4703), and a line still more refrangible than the hitherto recorded lines, with wave-length 4354, were still more expanded each time that magnesium was added. These last two lines expanded much more on their less refrangible than on their more refrangible sides, and were not seen reversed. The bright blue line (wave-length 4481) seen when the spark is used, was not visible either bright or reversed; and this seems to be in agreement with Capron's photographs, which shew this line very strong with the spark but not with the arc.

The following experiments were made in carbon crucibles:—

When strontia was put in the lines with wave-lengths 4607, 4215 and 4079 were all seen with dark lines in the middle, but no reversal of any strontium line less refrangible could be seen. After adding some aluminium and some potassium carbonate to increase the current of vapour, no reversal

of any strontium red line could be detected, though momentary cloudy dark bands were seen in the red when fresh strontia was thrown in. Two dark lines were seen in the extreme red, which proved to be the potassium lines reversed (wave-lengths 7670 and 7700).

With a mixture of barium and potassium carbonates the line with wave-length 5535 was strongly reversed, and that with wave-length 4933 distinctly so. When barium chlorate was dropped into a crucible, the four lines with wave-lengths 4553, 4933, 5535, and 5518, were reversed, and as they remained so for some time, it is probable that the action of the oxygen of the chlorate had nothing to do with the result. The last-named line (5518) was the least strongly reversed.

To observe particularly the effects of potassium a mixture of lime and potassium carbonate previously ignited was thrown in. The violet lines of potassium, wave-length 4044, came out immediately as a broad black band, which soon resolved into *two* narrower dark bands having wave-lengths nearly 4042 and 4045. On turning to the red end the two extreme red lines were both seen reversed. No lines of potassium between the two extremes could be seen reversed, but the group of three yellow lines were all expanded though not nebulous, and other lines in the green were seen much expanded. These observations on potassium were more than once repeated with the same results.

Using sodium carbonate only the D lines were seen reversed though the other lines were expanded, and the pairs in the green had each become a very broad nebulous band, and D almost as broad a black band. When sodium chlorate was dropped into a crucible, the pair of lines with wave-lengths 5681, 5687 were both momentarily reversed, the latter much more strongly than the former.

When a very little charred rubidium tartrate was put in, the two violet lines were sharply reversed, appearing only as black lines on a continuous light background. Turning to the red end, the more refrangible of the two lines in the extreme red (wave-length 7800) was seen to have a decided dark line in the middle, and it continued so for some time. The addition of more rubidium failed to cause any reversal of the extreme red line, or of any but the three lines already mentioned.

On putting some lithium carbonate into the crucible, the violet line of lithium appeared as a nebulous band, and on adding some aluminium this violet band became enormously expanded, but shewed no reversal. The blue lithium line (wave-length 4604) was well reversed, as was also the red line, while a fine dark line passed through the middle of the orange line. On adding now a mixture of aluminium filings, and carbonates of lithium and potassium, the red line became a broad black band, and the orange line was

well reversed. The green line was exceedingly bright, but not nebulous or reversed, and the violet line still remained much expanded, but unreversed. With regard to the green lithium line, we may remark that we have no doubt whatever that it belongs to lithium, and that there must have been some mistake in Thalén's observation, which ascribed it to cæsium. We have never detected this line with cæsium, which, on the other hand, seems always to give the characteristic blue lines, both in the spark and in the flame, as well as to give the same lines reversed when its vapour is used as an absorbent.

When metallic indium was introduced into the crucible, both the lines with wave-lengths 4101 and 4509 were at once seen strongly reversed, and so continued for some time. No other absorption line of indium could be detected.

It is apparent that the expansion of lines, so often observed when fresh materials are introduced, must be ascribed to increase in the density of the vapours, not to any increase of temperature. Moreover, the length of tube which reaches a very high temperature in the experiments above described is very short in the lime crucibles, and still shorter in the carbon crucibles, so that the reversing layer is also short in many cases. We are, therefore, directing our attention to the means of heating up a longer length of the tubes, either by introducing oxy-hydrogen jets, or additional electric arcs one above another; and also to the introduction of reducing gas (hydrogen or carbonic oxide) to counteract the oxidising action of the air which is drawn in through the lateral openings.

The curious behaviour of the lines of different spectra with regard to reversal has induced us to compare the bright lines of the chromosphere of the sun, as observed by Young, with those that are reversed in our crucibles. It is well known that some of the principal lines of metals giving comparatively simple spectra, such as lithium, aluminium, strontium, and potassium, are not represented amongst the dark lines of Fraunhofer, while other lines of those metals are seen: and an examination of the bright chromospheric lines shews that special rays, highly characteristic of bodies which appear from other rays to be present in the chromosphere, are absent, or are less frequent in their occurrence than others.

In the following tables the relation between our observations on reversals and Young's on the chromospheric lines is shown.

In a subsequent communication we intend to examine carefully the contents of these tables. In the meantime we may remark that the group calcium, barium, and strontium, on the one hand, and sodium, lithium, magnesium, and hydrogen, on the other, seem to behave in a similar way in the chromosphere of the sun.

Lines in wave-lengths	Frequency in chromosphere	Behaviour. Reversal in our tubes	Remarks
Sodium 6,160 6,154 D 5,687 5,681 5,155 5,152 4,983 4,982	0 50 2 2 0	Expanded Most easy Difficultly reversed Very diffused " "	Principal ray
Lithium 6,705 6,101 4,972 4,603 4,130	0 3 0 0 0	Reversed Difficultly reversed 0 Readily reversed Very diffused	Most characteristic, at low temperature and low density Described by Boisbaudran
Magnesium 5,527 b ₁ 5,183 b ₂ 5,172 b ₄ 5,167 4,703 ? 4,586 4,481	40 50 50 30 0 0 0	Expanded Reversed " Difficultly reversed Much expanded " " Not seen either bright or reversed	} Most characteristic Doubtful whether due to magnesium Characteristic of spark absent in arc
Barium 6,677 6,496 6,140 5,534 5,518 4,933 4,899 4,553	25 18 25 50 15 30 30 10	0 0 0 Readily reversed Reversed " 0 Pretty readily reversed	May be either Ba or Sr May be either Ba or Sr Most persistent Well-marked ray
Strontium 6,677 6,496 4,607 4,215 4,077	25 18 0 40 25	0 0 Readily and strongly reversed Readily reversed " "	May be Sr or Ba Most "characteristic" Well marked "
Calcium 6,161 6,121 5,587 5,188 4,587 4,576 4,453	8 5 2 10 2 4 0	Reversed difficultly " " Doubtful reversal Reversed 0 0 Readily reversed	Very bright

Lines in wave-lengths		Frequency in chromosphere	Behaviour. Reversal in our tubes	Remarks
Calcium (<i>cont.</i>)	4,435	1	Readily reversed	Very characteristic
	4,425	2	"	
	4,226	3	Most easily reversed	
	4,095 (?)	0	Strongly reversed	
	3,968	75	Well reversed	
	3,933	50	Rather more readily than the last	
Aluminium	6,245	8	0	Strong lines
	6,237	8	0	
	3,961	0	Strongly reversed	Very marked
	3,943			
Potassium	7,670	0	Strongly reversed	Chief rays
	7,700			
	4,044	3		Well marked
	4,042			
Cæsium	5,990	10	0	Most marked
	4,555	10	Strongly reversed	

NOTE ON THE UNKNOWN CHROMOSPHERIC SUBSTANCE OF YOUNG

[*Proceedings of the Royal Society*, Vol. xxviii. (1879), p. 475]

IN the preliminary catalogue of the bright lines in the spectrum of the chromosphere published by Young in 1861, he calls special attention to the lines numbered 1 and 82 in the catalogue, remarking that "they are very persistently present, though faint, and can be distinctly seen in the spectro-scope to belong to the chromosphere, as such, not being due, like most of the other lines, to the exceptional elevation of matter to heights where it does not properly belong. It would seem very probable that both these lines are due to the same substance which causes the D_3 line."

Again, in a letter to *Nature*, June, 1872, Young says, "I confess I am sorry that the spectrum of iron shews a bright line coincident with 1474 (K); for, all things considered, I cannot think that iron vapour has anything to do with this line in the spectrum of the corona, and the coincidence has only served to mislead. But there are in the spectrum many cases of lines belonging to the spectra of different metals coinciding, if not absolutely, yet so closely, that no existing spectroscope can separate them, and I am disposed to believe that the close coincidence is not accidental, but probably points to some physical relationship, some similarity of molecular constitution perhaps, between the metals concerned....So, in the case of the green coronal matter, is it not likely that though not iron it may turn out to bear some important relation to that metal?" In 1876 he proves that the coronal line 1474 is not actually coincident with the line of iron.

In the catalogue of bright lines observed by Young at Sherman in the Rocky Mountains, to which we have directed special attention in one of our previous communications, it appears that the above-mentioned lines 1 and 82, along with D_3 , were as persistently present as hydrogen, the only other line approaching them in frequency of occurrence being the green coronal line 1474 of Kirchhoff, which was present on 90 occasions out of 100. It has occurred to us that these four lines may belong to the same substance. An analogy in the ratio of the wave-lengths of certain groups of lines occurring in different metals has been already pointed out by Stoney,

Mascart, Salet, Boisbaudran, and Cornu; and without any special reductions, or claims to an exact ratio in whole numbers, the following analogies are worthy of note:—

Hydrogen	Lithium	Magnesium	Chromospheric substance
Wave-length:—			
(1) 6563·9	(1) 6706	(1) 5183	(1) 7055 *
(2) 4862·1	(2) 6102	(2) 3837·8	(2) 5874·9
(3) 4340	(3) 4970	(3) 3335	(3) 5315·9
(4) 4102·4	(4) 4604		(4) 4471·2
	(5) 4130		
Ratio of wave-length of—			
(1) (2) & (4)	(1) (3) & (5)	(1) (2) & (3)	(1) (3) & (4)
$\frac{1}{20}$ $\frac{1}{27}$ $\frac{1}{32}$	$\frac{1}{20}$ $\frac{1}{26·9}$ $\frac{1}{32·5}$	$\frac{1}{20}$ $\frac{1}{27}$ $\frac{1}{31·1}$	$\frac{1}{20}$ $\frac{1}{26·5}$ $\frac{1}{31·6}$

The ratio of the wave-lengths of F to G of hydrogen ((2) to (3) in the table above) is nearly identical with the ratio of D₃ to the coronal green line ((2) to (3) in the last column of the table above).

This near coincidence in the ratios of certain lines of hydrogen, lithium, and magnesium, substances belonging to the same type, combined with a similar ratio in the wave-lengths of the nearly equally persistent lines of the chromosphere, greatly strengthens the probability of the assumption that these lines belong to one substance.

The fact that the two less refrangible rays have no representative in the Fraunhofer lines, is by no means opposed to their belonging to one substance, since we know that aluminium behaves in a similar way in the atmosphere of the sun; and in the total eclipse of 1875 the hydrogen line *h* was not visible in the chromosphere, that is, we suppose, was on the limit between brightness and reversal; and during the late eclipse the two most refrangible rays of hydrogen were not detected from the same cause.

Until our knowledge of the order of reversibility of lines belonging to different types of metals has been extended, it would be rash to infer the group of metals to which it belongs, or its probable molecular weight.

* This wave-length is not so accurately known as the other rays belonging to the chromosphere.

ON THE REVERSAL OF THE LINES OF METALLIC VAPOURS

[*Proceedings of the Royal Society*, Vol. xxviii. (1879), pp. 471 sqq.]

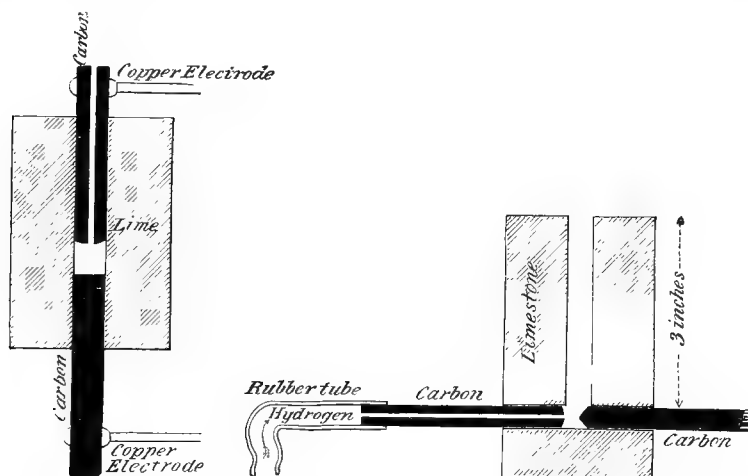
THE experiments described in the following communication were made with the electric arc, and in lime crucibles*, or in crucibles of a highly calcareous sandstone, kindly supplied to us by Messrs Johnson, Matthey, and Co., as described in our fourth communication on this subject; but for some of them we used, instead of a galvanic battery, a magneto-electric machine producing a much more powerful current and a much longer arc. The experiments with this machine were made, through the kindness of Dr Tyndall, at the Royal Institution, and we are indebted to Messrs Siemens both for the working of the machine and for sparing to us the services of a skilled engineer, in the person of Mr Oscar Doermer, whose assistance was most valuable. We wish to express our thanks to all these gentlemen for the facilities they so readily granted to us.

The results obtained with the powerful current from the magneto-electric machine did not differ at all in kind from those obtained with the battery, and much less in degree than we had expected. We had really but one day's work with this machine, which we can only regard as a preliminary trial of it, and, in the meantime, until we have the opportunity of a longer series of experiments with it, we communicate the results obtained to the Royal Society.

In some cases we have introduced a current of hydrogen, or of coal-gas, into the crucibles by means of a small lateral opening, or by a perforation through one of the carbon electrodes; sometimes the perforated carbon was

* In our first paper on this subject, communicated in February, 1878, when referring to the experiments of Lockyer and Roberts (*Proc. Roy. Soc.* Vol. xxiii), we mentioned that they employed the combined action of a charcoal furnace and an oxy-hydrogen blowpipe, but omitted to mention that they used a lime chamber after the model of Stas. Referring to fig. 1 in our fourth communication on this subject (p. 23), where the use of an oxy-hydrogen blowpipe in a lime block is represented, we disclaim any novelty in the use of lime; the difference between our experiments and theirs consisting in this, that we use the continuous spectrum from the hot walls of our crucible, instead of an external independent source of light, as a background against which the absorbent action of the vapours is seen, in the same way as we had previously used iron tubes, and now use the electric arc.

placed vertically, and we examined the light through the perforation (see diagrams). When no such current of gas is introduced, there is frequently a flame of carbonic oxide burning at the mouth of the tube, but the current of hydrogen produces very marked effects. As a rule, it increases the brilliancy of the continuous spectrum, and diminishes relatively the apparent intensity of the bright lines, or makes them altogether disappear with the exception of the carbon lines. When this last is the case, the reversed lines are seen simply as black lines on a continuous background. The calcium line with wave-length 4226 is always seen under these circumstances as a more or less broad black band on a continuous background, and when the temperature of the crucible has risen sufficiently, the lines with wave-lengths 4434 and 4454, and next that with wave-length 4425, appear as simple black lines. So too do the blue and red lines of lithium, and the barium line of wave-length 5535, appear steadily as sharp black lines, when no



trace of the other lines of these metals, either dark or bright, can be detected. Dark bands also frequently appear, with ill-defined edges, in the positions of the well-known bright green and orange bands of lime.

In the case of sodium, using the chloride, we have repeatedly reversed the pair of lines (5687, 5681) next more refrangible than the D group. In every case the less refrangible of the two was the first to be seen reversed, and was the more strongly reversed, as has also been observed by Mr Lockyer. But our observations on this pair of lines differ from his in so far as he says that "the double green line of sodium shews scarcely any trace of absorption when the lines are visible," while we have repeatedly seen the reversal as dark lines appearing on the expanded bright lines; a second pair of faint bright lines, like ghosts of the first, usually coming out at the same time on the more refrangible side.

Using potassium carbonate, besides the violet and red lines which had been reversed before, we saw the group, wave-length 5831, 5802, and 5782, all reversed, the middle line of the three being the first to shew reversal. Also the lines wave-length 6913, 6946, well reversed, the less refrangible remaining reversed the longer. Also the group, wave-length 5353, 5338, 5319, reversed, the most refrangible not being reversed until after the others. Also the line wave-length 5112 reversed, while two other lines of this group, wave-lengths 5095 and 5081, were not seen reversed.

Using lithium chloride, not only were the red and blue lines, as usual, easily reversed, and the orange line well reversed for a long time, but also the green line was distinctly reversed; the violet line still unreversed, though broad and expanded. Had this green line belonged to cæsium, the two blue lines of that metal which are so easily reversed could not have failed to appear; but there was no trace of them.

In the case of rubidium, we have seen the less refrangible of the red lines well reversed as a black line on a continuous background, but it is not easy to get, even from the arc in one of our crucibles, sufficient light in the low red to shew the reversal of the extreme ray of this metal.

With charred barium tartrate, and also with baryta and aluminium together, we have obtained the reversal of the line with wave-length 6496, besides the reversals previously described. The less refrangible line, wave-length 6677, was not reversed.

With charred strontium tartrate, the lines with wave-lengths 4812, 4831, and 4873 were reversed, and by the addition of aluminium, the line wave-length 4962 was reversed for a long time, and lines wave-length 4895, 4868, about, were also reversed.

On putting calcium chloride into the crucible, the line wave-length 4302 was reversed, this being the only one of the well-marked group to which it belongs which appeared reversed. On another occasion, when charred strontium tartrate was used, the line wave-length 4877 was seen reversed, as well as the strontium line near it. Also the lines wave-length 6161, 6121 have again been seen momentarily reversed.

With magnesium, no new reversals of the lines of the metal have been observed by us; but when a stream of hydrogen or of coal-gas was led into the crucible, the line wave-length 5210, previously seen by us in iron tubes, and ascribed by us to a combination of magnesium with hydrogen, was regularly seen, usually as a dark line, sometimes with a tail of fine dark lines on the more refrangible side similar to the tail of bright lines seen in the sparks taken in hydrogen between magnesium points. Sometimes, however, this line (5210) was seen bright. It always disappeared when the gas was discontinued, and appeared again sharply on re-admitting the hydrogen.

These effects were, however, only well-defined in crucibles having a height of at least 3 inches above the arc.

On putting a fragment of metallic gallium into a crucible, the less refrangible line, wave-length 4170, came out bright, and soon a dark line appeared in the middle of it. The other line, wave-length 4031, shewed the same effect, but less strongly.

In the cases of cadmium and copper, though we have made no thorough examination of them, we can corroborate the results arrived at by Cornu. We noticed particularly the disappearance in the arc of the cadmium lines, with wave-lengths 5377 and 5336.

On the addition of aluminium to either copper or silver in our lime crucibles, we noticed that the copper or silver lines which had been previously predominant, almost faded away, while the calcium lines came out instead with marked brilliancy. In no case could we detect the red lines of aluminium in the arc.

With a view to re-introduce into the arc the magnesium line wave-length 4481, we tried the action of an induction spark in a lime crucible simultaneously with the arc, but without success; for the conducting power of the hot walls of the crucible, and the highly expanded gases within it, caused the resistance to be so much diminished, that the spark passed as in a highly rarefied medium. In order to succeed with this experiment, it seems plain that it must be made in an apparatus which will allow of its being performed under a pressure of several atmospheres.

Reviewing the series of reversals which we have observed, we may remark that in many cases the least refrangible of two lines near together is the most easily reversed, as has been previously remarked by Cornu. Thus, in the case of barium (though there is no very distinct grouping of the lines of that metal), taking the rays in order, we have the line wave-length 5535 readily reversed, while that with wave-length 5518 is less easily reversed; the line wave-length 4933 is comparatively easily reversed, whereas that with wave-length 4899 has not been reversed by us. On the other hand, the line wave-length 4553 has been reversed, but not the line wave-length 4524. In the case of strontium, the lines wave-length 4831 and 4812 have been reversed, but not the line wave-length 4784, and the two lines wave-length 4741 and 4721 remain both unreversed. In the group of five lines of calcium, wave-length 4318 to 4282, it is only the middle line wave-length 4302 which has been reversed. Of the potassium group of lines wave-length 5831 to 5782, 5802 and 5782 are reversed, the line wave-length 5811 has not been reversed, and of the others the line wave-length 5802 is the first to appear reversed. It is worthy of remark that the first of these lines is faint and the last is the brightest of the group. The group wave-lengths 5355, 5336, 5319 have been all reversed, but the last of the three (5319) was the most

difficult to reverse: it is also the feeblest of the group. In the more refrangible group, wave-length 5112, 5095, 5081, the least refrangible is the only one reversed.

Making a general summation of our results respecting the alkaline earth metals, potassium, and sodium, and having regard only to the most characteristic rays, which for barium we reckon as 21, for strontium 34, for calcium 37, for potassium 31, and for sodium 12, the reversals in our experiments number respectively 6, 10, 11, 13, and 4. That is, in the case of the alkaline earth metals, about one-third, and these chiefly in the more refrangible third of the visible spectrum, the characteristic rays remaining unreversed in the more refrangible part of the spectrum being respectively 2, 5, and 4. In the case of potassium we reversed two in the upper third, all the rest in the least refrangible third. These experiments relate to mixtures of salts of these metals combined with the action of reducing agents. In a future communication we will contrast these results with those of the isolated metals, calcium, strontium and barium.

NOTE ON A DIRECT VISION SPECTROSCOPE AFTER THOLLON'S
PLAN, ADAPTED TO LABORATORY USE, AND CAPABLE OF
GIVING EXACT MEASUREMENTS

[*Proceedings of the Royal Society*, Vol. XXVIII. (1879), p. 482]

HAVING seen in the *Journal de Physique* for May, 1878, the account of M. Thollon's ingenious direct vision spectroscope, it occurred to us that by a little modification we could adapt his plan so as to produce an instrument well fitted for the work in which we were engaged, combining the advantage of excellent definition, which his plan secures, with the means of getting exact measurements with the least possible chance of errors of adjustment or inequalities in the working of the automatic system. The principle consists in having two prisms only (half-prisms as M. Thollon calls them), of which one is fixed, and receives the light from the collimator by a reflecting prism and transmits it in a plane at right angles to the axis of the collimator to the second prism.

This second prism is moveable about an axis parallel to its edge and to the axis of the telescope, and has a right-angled reflecting prism attached to it, so that the light after traversing this prism twice passes the second time through the fixed prism and so by reflection into the telescope. The lever carrying the second prism with its reflecting prism is moved by a micrometer screw, by the head of which the movement of the prism is read.

We placed the design in the hands of Mr Hilger, some time since, and we now exhibit the instrument to the Society.

In the last number of the *Journal de Physique*, M. Thollon describes some modification of his instrument, but it does not seem that his modified plan is so well adapted to the ordinary use of a chemical laboratory as ours.

The accompanying diagram, No. 1, represents a section through the prisms at right angles to the axis of the collimator and telescope.

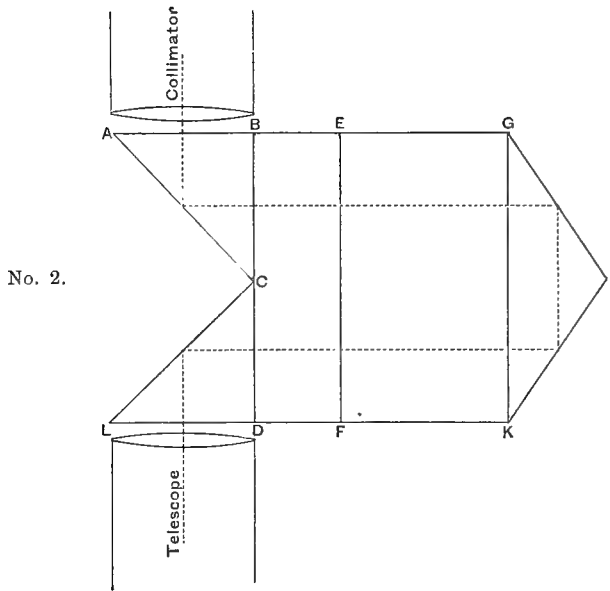
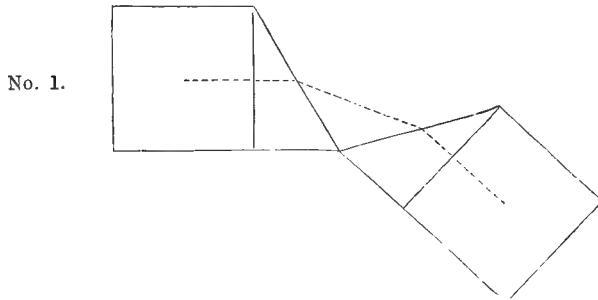


Diagram No. 2 (not in the original paper but given by Kayser, *Handbuch der Spectroscopie* i 521) shews the projection of the prisms on a plane through EF , the axis of the moveable part, perpendicular to the edges of the fixed reflecting prisms.

ABC and CLD fixed reflecting prisms.

$BEFD$ fixed refracting prism.

$EGKF$ moveable refracting prism.

GIK reflecting prism attached to $EGKF$.

The dotted line indicates the course of a ray of light through the instrument.

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ON THE DISPERSION OF A SOLUTION OF MERCURIC IODIDE

[*Proceedings of the Cambridge Philosophical Society*, Vol. III. Pt vi.
(1879), p. 258]

IN the *Chemical News*, Vol. xxix, p. 128, Mr E. Sonstadt proposes the use of a solution of mercuric iodide combined with potassium iodide as a convenient liquid for testing specific gravities, and mentions that he has obtained it with a specific gravity upwards of three times that of water. Being in search of a substance which would give a considerable dispersion of the red end of the spectrum I thought I would try the dispersive power of this solution; and though its power of dispersing the red is not nearly so great as its power of dispersing the green, its dispersive power is still very remarkable throughout the range of colours which it transmits. My assistant, Mr Robinson, has prepared the solution for me, but though he has obtained it of sp. gr. 3.013 at a temperature of 17° C. since the observations described below were made, the liquid of which I have examined the dispersion is of sp. gr. 2.77 at 18° C. It is of a pale yellow colour, and seems to absorb completely the violet and indigo light. On observing the solar spectrum through it there is no perceptible diminution of light until nearly half-way between *F* and *G*; the absorption begins there, and thence increases very rapidly. At the red end *A* could be seen, so there is not much absorption of visible rays of low refrangibility.

Filling a hollow prism of 59° 11' with the liquid, I obtained the following indices of refraction:

<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>
1.628	1.637	1.641	1.654	1.673	1.693

Taking *E* as the standard ray, I get for the dispersive power $\left(\frac{\mu_2 - \mu_1}{\mu_0 - 1}\right)$ between

<i>A—B</i>	<i>B—D</i>	<i>D—E</i>	<i>E—F</i>
.01263	.02555	.02822	.02896

Comparing these figures with those given in Watts' *Dictionary* for dense flint-glass and for carbon disulphide, we have refractive indices

	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>
Flint-glass		1·6278	1·6297	1·6350	1·6420	1·6483
CS^2 at 11°	1·6142	1·6207		1·6333	1·6465	1·6584

giving dispersive powers

	<i>A—B</i>	<i>B—D</i>	<i>D—E</i>	<i>E—F</i>
Flint-glass		·01134	·01089	·00972
CS^2	·01005	·01949	·02042	·01841

The dispersive power of the mercury solution is therefore very nearly three times that of flint-glass for green light and more than double for orange light: and it is more than one-half greater than that of carbon disulphide for green light, and nearly one-third greater for orange light. So the green part of the spectrum is in comparison with the red even more drawn out by the mercury solution than by carbon disulphide. The figures above given depend only on one set of observations, and are therefore open to correction by future examination.

ON A NEW SPECTROSCOPE

[*Proceedings of the Cambridge Philosophical Society*, Vol. III. Pt vi.
(1879), p. 260]

THE aim of this instrument is to obtain considerable dispersion with as little loss of light as possible, and at the same time good definition in all parts of the spectrum. Young has pointed out the economy of using one half-prism attached to the collimator with one face perpendicular to the axis, and another similar half-prism attached in a similar way to the telescope. A beam of light can thus be used larger, in proportion to the size of the face of the prism, than when a single prism with an angle equal to the sum of the angles of the half-prisms is used. Thollon has given a mathematical investigation to shew that when two half-prisms are thus used and the incident and emergent light is normal to the first and last faces of the pair respectively, the deviation is a minimum. It is, however, easy to see without analysis that two prisms of 30° placed as in fig. 1, so as to be equivalent to a single prism of 60° at minimum deviation, have the angles of incidence and refraction the same as when they are placed as in fig. 2, only these angles occur in a different order. The deviation will be the same in each case, and there will be equal clearness of definition. In the spectro-

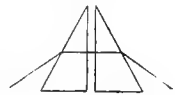


FIG. 1.



FIG. 2.

With so great a dispersion as these two whole and two half-prisms give, it is necessary to adjust the prisms to minimum deviation, or nearly so, in order to get good definition, or even to see faint lines at the extremities of the spectrum. In order, therefore, to be able to use it for the kind of work in which the author has, in conjunction with Professor Dewar, been for some time past engaged, which often involves a rapid transition from one end of the spectrum to the other, some automatic adjustment of the prisms was

desirable. This is effected by a simple system which cannot easily go wrong. The collimator *L*, see fig. 3, is fixed to the table of the instrument so that the prolongation of the first face of the half-prism attached to it may pass through the centre of the table; a broad arm *E*, turning on an axis *C* at the centre of the table, carries the telescope *T* and a vernier by which the angle through which the telescope is turned can be read upon the graduated rim of the table. The two whole prisms are each carried by an arm moveable about the same axis *C* as the telescope. The plane through the edge of the first prism *A* and the axis *C* is made always to bisect the angle between the

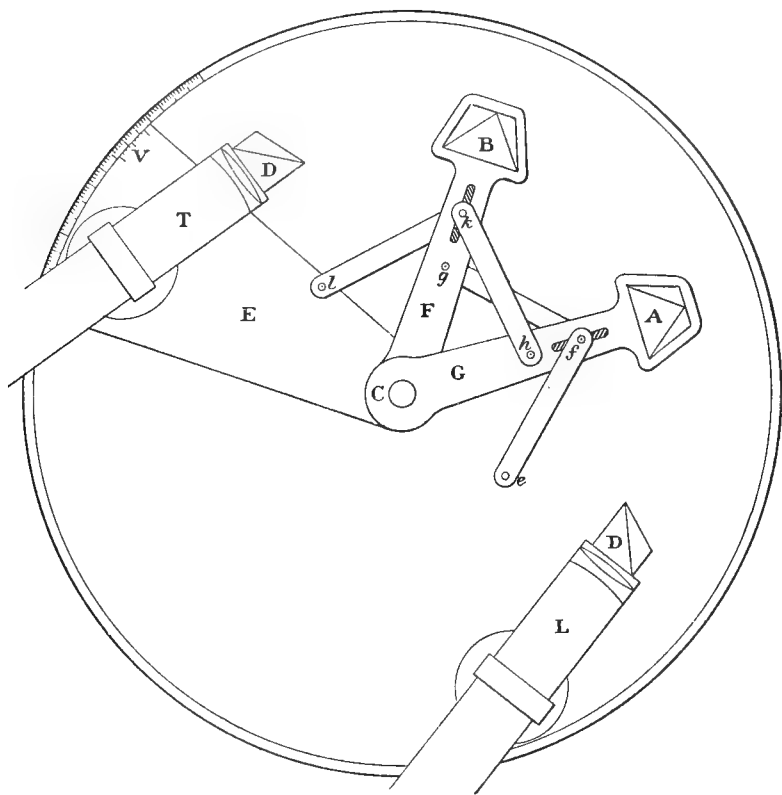


FIG. 3.

plane through the edge of *B* and the same axis and the plane which is the prolongation of the first face of the half-prism attached to the collimator. This is effected by two levers, one working on a pivot *e* fixed to the table, and the other working on a pivot *g* fixed to the arm *F* which carries the prism *B*. These two levers have at their other ends a common pivot *f*, which works in a slot in the arm *G* which carries the prism *A*. The line *CA* thus always bisects the angle *gCe*. By similar levers attached to the arms *E* and *G* the line *BC* is made always to bisect the angle *lCh*. By this

mechanism the prisms are always kept symmetrically arranged. Measurements are taken by moving the telescope until the line to be measured is on the cross wires of the telescope. It is not of any consequence in practice whether the prisms be always exactly at the minimum deviation, provided they be nearly so, but it is important, where measures are taken by readings of the angle through which the telescope is moved, that the readings should always be the same when the same line is on the cross wires. To ensure this the author purposes to have spiral springs attached to the several moveable arms, so as to keep them always up to their bearings on one side. The instrument has been made by Browning. Were another such instrument constructed it might perhaps be well to replace the flat arm with a slot which may wear to uneven edges, by an arm with its middle part square in section and a tube sliding on it to which the levers should be hinged as in fig. 4. The wear in this case would be more uniform and of less consequence.

To illuminate the cross wires when the field is dark the author proposes to place a small collimator, with a pin-hole instead of a slit, so that the light from it may be reflected from the second face of the second prism. Since the angle through which this prism moves

is always half that through which the telescope is moved the image of the pin-hole will be in a nearly constant position in the field of view; and it may be conveniently illuminated by a sodium flame.

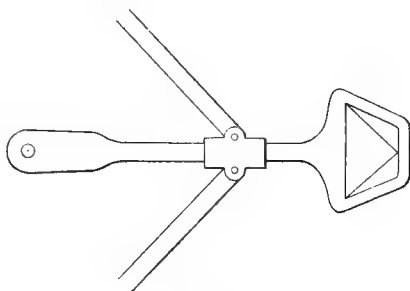


FIG. 4.

NOTE ON "SPECTROSCOPIC PAPERS"

[*Proceedings of the Royal Society*, Vol. xxix. (1879), p. 166]

IN a recent communication to the Royal Society, Mr Lockyer has criticised our statement of Young's wave-length identifications of certain chromospheric lines. As to the wave-length, we have throughout our table omitted all figures after the decimal point merely for the sake of not cumbering the table. The numbers, Young tells us, are not his own, but taken from Ångström's catalogue. Moreover, as to Young's identifications with metallic lines, he states expressly that they were taken from the maps of Kirchhoff, Ångström, and Thalén, and Watts' *Index of Spectra*. But our object was not to criticise Young's work, but only to use it for the purpose of comparing the behaviour of certain metals on the earth and in the sun, and the conditions under which certain lines appear, or do not appear, or are reversed.

We should perhaps have made our meaning clearer if we had given another column with the wave-lengths of the metallic lines referred to side by side with Young's numbers for the chromospheric lines. We mentioned, in relation to aluminium, the two lines with wave-lengths 6245·4 and 6237·3 seen by Young, not because we thought their identity with the aluminium lines proved, but because they are the only two lines in Young's table which are at all close to aluminium lines, and if they be not due to that metal, then we have the remarkable fact that aluminium in the sun gives no lines either dark or bright except the two which have been reversed on the earth. A somewhat similar remark applies to the potassium lines, only in that case Young's line has a wave-length very nearly the mean of the two potassium lines which are often seen as one, not merely from want of dispersive power (which with prisms is usually sufficient at the violet end), but because the lines are expanded until they meet. We at first saw them reversed as one broad line which divided in two as the potassium evaporated.

Mr Lockyer complains that we omitted to refer to his work on the wave-length of the potassium lines. In our first communication on the subject of reversals we named at the outset those who had been previously engaged in the same field, and after referring to their work in general terms we did not think it desirable subsequently to notice the specific results obtained by each individual. As neither the existence of the two potassium lines nor the exact determination of their wave-lengths, but only the identification of the dark

lines we observed with the bright lines was in question, we considered it unnecessary to mention specially Mr Lockyer's work on those lines.

We owe it to the Society to explain the value which is to be attached to the wave-lengths mentioned by us. We have never set ourselves to determine exact wave-lengths; but we sought to determine the conditions of reversal, and we used wave-lengths for the convenience of indicating the lines of which we wrote. In very few cases have we given any determinations of wave-lengths. In general we determined the identity of a dark line with the corresponding bright line by observing that both had the same place on the cross wires, or pointer, or both gave the same reading of the scale of the spectroscope. We then gave the wave-length of the bright line as determined by some good authority, usually either Thalén or Boisbaudran. When we could not identify the dark lines in that way, we took the readings of known lines with our spectroscope, using, for lack of sunshine, most frequently Boisbaudran's method and wave-lengths, and having drawn a curve, determined the wave-lengths of the dark lines therefrom. It was in this way that we obtained the wave-lengths of the two dark lines we ascribed to potassium. It is, of course, just within the bounds of possibility that the line for which we obtained the wave-length 4045 (it is misprinted 4,044 in the table, but not in the text) may have been an iron line reversed, but, as the principal well-known lines of potassium were at the same time seen bright in the spectrum while those of iron were not seen, it is far more probable, almost certain, that the line was really due to potassium, and the last figure of the wave-length wrongly determined. By giving exactly what we observed, we have enabled our readers to judge for themselves what is most probable in this case. To attempt to determine wave-lengths to any greater degree of nicety would, so far as our purpose was concerned, have been labour thrown away. Whenever the wave-length of a line observed by us to be reversed is given differently from that given by Thalén and that given by Boisbaudran for the bright line to which we assume it to correspond, it was determined in the way above described, and must not be taken to have more importance. By our method of working, the very high dispersive power required for the specific identification of any substance by the determination of an individual wave-length is avoided; as we depend on the greatly diminished likelihood of error when several groups of lines of the same substance are seen to be continually present at the time of one or more reversals. It was the necessity of being able to rapidly sweep the entire spectrum for the above purpose that caused us to limit the dispersion. A large majority of the wave-lengths given by Thalén were obtained by means of the moderate dispersion of one bisulphide of carbon prism, a less dispersion than we have used; and it would be incorrect to suppose that no enduring work in this field of spectroscopy can be effected except with the enormous dispersive power which Mr Lockyer recommends.

SPECTROSCOPIC INVESTIGATION

[*Proceedings of the Royal Institution*, Vol. ix. (1879), pp. 204–220]

IN Kirchhoff's celebrated paper "On the Relation between the Radiating and Absorbing Powers of different Bodies for Light and Heat," the remarkable experiments of reversing the bright lines of lithium and sodium by causing sunlight to pass through the vapours of those metals, volatilized in the flame of a Bunsen's burner, are described. Bunsen and Kirchhoff reversed the stronger lines of potassium, calcium, strontium, and barium by deflagrating their chlorates with milk-sugar, before the slit of the solar spectroscope. Recent researches on the artificial formation of Fraunhofer lines have been made by Cornu, Lockyer, and Roberts.

Cornu improved upon a method previously used by Foucault. It depends upon so arranging the electric arc that the continuous spectrum of the intensely heated poles is examined through an atmosphere of the metallic vapours volatilized around them. By this means Cornu succeeded in reversing several lines in the spectra of the following metals, in addition to those above mentioned, viz. thallium, lead, silver, aluminium, magnesium, cadmium, zinc, and copper. He observed that, in general, the reversal began with the least refrangible of a group of lines, and gradually extended to the more refrangible lines of the group, and drew the conclusion that a very thin layer of vapour was sufficient for the reversal. In almost every case the lines reversed are the more highly refrangible of the lines characteristic of each metal.

Lockyer's plan was to view the electric arc through the vapours of the metals volatilized in a horizontal iron tube. The iron tube had its ends covered with glass plates, and was heated in a furnace, a current of hydrogen passing during the experiment. He did not succeed in observing any new reversal of bright lines, with the exception of an unknown absorption line which sometimes appeared when zinc was experimented on. He confirmed, however, the channelled-space absorption spectra observed by Roscoe and Schuster in the cases of potassium and sodium, and recorded channelled-space spectra in the case of antimony, phosphorus (?), sulphur, and arsenic (probably). "As the temperature employed for the volatilization of the

metals did not exceed bright redness, or that at which cast iron readily melts, the range of metals examined was necessarily limited; and in order to extend these observations to the less fusible metals, as well as to ascertain whether the spectra of those volatilized at the lower temperature would be modified by the application of a greater degree of heat," a new series of experiments were undertaken by Lockyer and Roberts, in which the combined action of a charcoal furnace and the oxy-hydrogen blowpipe was employed. A lime crucible after the form of Stas was used to replace the iron tube. By this means they obtained still no new reversal of a metallic line, but they observed channelled-space spectra in the cases of silver, manganese, chromium, and bismuth. They observed, however, that the metal thallium gave the characteristic *bright green* line, the light of the arc not being reversed.

In the above-mentioned experiments, the coolness of the ends of the tube, which acted as condensers of the metallic vapours, and the continual change of density and temperature necessarily produced by the maintenance of a current of hydrogen through the tube, appear to account for the failure in observing reversals.

The following facts have been acquired during the course of a long series of conjoint experiments with my distinguished colleague, Professor Liveing, of Cambridge*.

In order to examine the reversal of the spectra of metallic vapours, it is more satisfactory to observe the absorptive effect produced on the continuous spectrum emitted by the sides and end of the tube in which the volatilization takes place. For this purpose it is convenient to use iron tubes about half an inch in internal diameter, and about 27 inches long, closed at one end, thoroughly cleaned inside, and coated on the outside with borax, or with a mixture of plumbago and fireclay. These tubes are inserted in a nearly vertical position in a furnace fed with Welsh coal, which will heat about 10 inches of the tube to about a welding heat, and observations are made through the upper open end of the tube, either with or without a cover of glass or mica. To exclude oxygen, and avoid as much as possible variations of temperature, hydrogen is introduced in a gentle stream by a narrow tube into the upper part only of the iron tube, so that the hydrogen floats on the surface of the metallic vapour without producing convection currents in it. By varying the length of the small tube conveying the hydrogen, the height in the tube to which the metallic vapour reaches may be regulated. Thus different depths of metallic vapour may be maintained at a comparatively constant temperature for considerable

* "On the Reversal of the Lines of Metallic Vapours," Nos. I., II., III., IV., V., VI., *Proc. Roy. Soc.*, 1878-1879.

periods of time. The general plan of the apparatus is given in the diagram on page 9.

By this means the characteristic lines of the volatile metals thallium and indium may be easily reversed.

Metallic lithium, alone or mixed with sodium, gave no results. Similarly, chloride of lithium and metallic sodium, introduced together, gave no better results. To a tube containing mixed potassium and sodium vapour, lithium chloride was added. Now the bright-red lithium line was sharply reversed, and remained well-defined for a long time. The lithium line was only reversed in a mixture of the vapours of potassium and sodium, and it seems highly probable that a very slightly volatile vapour may be diffused in an atmosphere of a more volatile metal, so as to secure a sufficient depth of vapour to produce a sensible absorption. This would be analogous to well-known actions which take place in the attempt to separate organic bodies of very different boiling points by distillation, where a substance of high boiling point is always carried over, in considerable quantity, with the vapour of a body boiling at a much lower temperature.

Sodium and potassium, when observed in such tubes, give none of the appearances noted by Lockyer, "On a New Class of Absorption Phenomena," in the *Proceedings of the Royal Society*, Vol. xxii, but the channelled-space spectrum of sodium described by Roscoe and Schuster in the same volume of the *Proceedings* was often seen. Potassium gives no channelled-space absorption, but continuous absorption in the red, and one narrow absorption band, with a wave-length of about 5730, not corresponding with any bright line of that metal.

The absorption spectrum of sodium vapour is by no means so simple as has been generally represented. The fact that the vapour of sodium in a flame shews only the reversal of the D lines, while the vapour, volatilized in tubes, shews a channelled-space absorption corresponding to no known emission spectrum, appears to be a part of a gradational variation of the absorption spectrum, which may be induced with perfect regularity. Experiments with sodium exhibit the following succession of appearances, as the amount of vapour is gradually diminished, commencing from the appearance when the tube is full of the vapour of sodium, part of it condensing in the cooler portion of the tube, and some being carried out by the slow current of hydrogen. During this stage, although the lower part of the tube is at a white heat, as long as the cool current of hydrogen displaced metallic vapour, on looking down the tube it appeared perfectly dark. The first appearance of luminosity is of a purple tint, and, with the spectroscope, appears as a faint blue band, commencing with a wave-length of about 4500, and fading away into the violet. Next appears a narrow band in the green, with a maximum of light having a wave-length of about

5420, diminishing in brightness so rapidly on either side as to appear like a bright line. This green band gradually widens, and is then seen to be divided by a dark band with a wave-length of about 5510. Red light next appears, and between the red and green light is an enormous extension of the D absorption line, while a still broader dark space intervenes between the green and the blue light. The dark line in the green (wave-length about 5510) now becomes more sharply defined. This line appears to have been observed by Roscoe and Schuster, and regarded by them as coinciding with the double sodium line next in strength to the D lines, but it is considerably more refrangible than that double line. In the next stage, the channelled-space spectrum comes out in the dark space between the green and blue, and finally in the red. Gradually the light extends, the channels disappear, the D lines absorption narrows, but still the dark line in the green is plainly discernible. Lastly, there is only D lines absorption.

The method of observation described may be used to observe emission as well as absorption spectra; for if the closed end of the tube be placed against the bars of the furnace so as to be relatively cooler than the middle of the tube, the light emitted by the vapours in the hottest part is more intense than that emitted by the bottom of the tube. This succeeds admirably with sodium.

The volatility of rubidium and caesium rendered it advisable to try the effects first in glass tubes. For this purpose a piece of combustion tubing had one end drawn out and the end turned up sharply, and sealed off (like an ill-made combustion tube of the usual form), so as to produce an approximately plane face at the end of the tube; a small bulb was then blown at about an inch from the end, and the tube drawn out at about an inch from the bulb on the other side, so as to form a long narrower tube. Some dry rubidium or caesium chloride was introduced into the bulb, and a fragment of fresh cut sodium, and the narrow part of the tube turned up, so as to allow the tube and bulb to be seen through in the direction of the axis of the tube. The shape of tube is given in the diagram on page 9. The open end was then attached to a Sprengel pump, and the air exhausted; the sodium was then melted, and afterwards either dry hydrogen or dry nitrogen admitted, and the end of the tube sealed off at nearly the atmospheric pressure. It was necessary to have this pressure of gas inside the tube, otherwise the metal distilled so fast, on heating, that the ends were speedily obscured by condensed drops of metal. Through these tubes placed lengthways in front of a spectroscope, a lime light was viewed. On warming the bulb of a tube in which rubidium chloride had been sealed up with sodium, the D lines were of course very soon seen; and very soon there appeared two dark lines near the extremity of the violet light, which, on measurement, were found to be identical in position with the well-known violet lines of rubidium. Next appeared faintly the channelled spectrum of sodium in the green,

and then a dark line in the blue, very sharp and decided, in the place of the more refrangible of the characteristic lines of cæsium in the flame spectrum. As the temperature rose, these dark lines, especially those in the violet, became sensibly broader; and then another fine dark line appeared in the blue, in the place of the less refrangible of the cæsium blue lines. During this time no dark line could be observed in the red; but as the temperature rose, a broad absorption band appeared in the red, with its centre about midway between B and C, ill-defined at the edges, and though plainly visible not very dark. The lines in the violet had now become so broad as to touch each other and form one dark band. On cooling, the absorption band in the red became gradually lighter without becoming defined, and was finally overpowered by the channelled spectrum of sodium in that region. The double dark line in the violet became sharply defined again as the temperature fell. There are two blue lines in the spectrum of rubidium taken with an induction-coil very near the two blue lines of cæsium; but they are comparatively feeble, and the two dark lines in the blue observed in the places of the characteristic blue lines of cæsium must have been due to a small quantity of cæsium chloride in the sample of rubidium chloride. These blue lines were not, however, visible when some of the rubidium chloride was held in the flame of a Bunsen's burner, nor when a spark was taken from a solution of the chloride; but the more refrangible of them (Cs_2) was visible in the spark of an induction-coil, without a Leyden jar, taken between beads of the rubidium chloride fused on platinum wires.

When a tube containing cæsium chloride and sodium was observed, in the same way, the two dark lines in the blue were seen very soon after the heating began, and the more refrangible of them broadened out very sensibly as the temperature increased. The usual channelled spectrum of sodium was seen in the green, and an additional channelling appeared in the yellow, which may be due to cæsium or to the mixture of the two metals. Indeed the cæsium chloride was not free from rubidium, and the dark lines of rubidium were distinctly seen in the violet. Metallic lithium acts on the chlorides of cæsium and rubidium, giving the same results as sodium.

It is remarkable that these absorption lines of cæsium coincide with the blue lines of cæsium as seen in the flame, not with the green line which that metal shews when heated in an electric spark of high density. It is to be observed, however, that when sparks from an induction-coil without a jar are taken between beads of cæsium chloride fused on platinum wires, a spectrum similar to the flame spectrum is seen, and it is only when a Leyden jar is used that the spectrum is reduced to a green line. In like manner both the violet lines of rubidium are reversed, and both these violet lines are seen when the spark of an induction-coil, without jar, is passed

between beads of rubidium chloride fused on platinum wire, though only one of them appears when a Leyden jar is used.

Mixtures of carbonate of cæsium with carbon, and of carbonate of rubidium with carbon, prepared by charring the tartrates, heated in narrow porcelain tubes, placed vertically in a furnace, gave sharp results. A small quantity of the cæsium mixture, introduced into a tube at a bright red heat, shewed instantly the two blue lines reversed and so much expanded as to be almost in contact. The width of the dark lines decreased as the cæsium evaporated, but they remained quite distinct for a long time. A similar effect was produced by the rubidium mixture, only it was necessary to have the tube very much hotter, in order to get enough of violet light to see the reversal of the rubidium lines. In this case the two lines were so much expanded as to form one broad dark band, which gradually resolved itself into two as the rubidium evaporated. The reversal of these lines of cæsium and rubidium seems to take place almost or quite as readily as that of the D lines by sodium, and the vapours of those metals must be extremely opaque to the light of the refrangibility absorbed, for the absorption was conspicuous when only very minute quantities of the metals were present. The red, yellow, and green parts of the spectrum were carefully searched for absorption lines, but none due to cæsium or rubidium could be detected in any case. It is perhaps worthy of remark that the liberation of such extremely electro-positive elements as cæsium and rubidium from their chlorides by sodium and by lithium, though it is probably only partial, is a proof, if proof were wanting, that so-called chemical affinity only takes a part in determining the grouping of the elements in such mixtures; and it is probable that the equilibrium arrived at in any such case is a dynamical or mobile equilibrium, continually varying with change of temperature.

It is difficult to prevent the oxidation of magnesium in the iron tubes, and tubes wider than half an inch did not give satisfactory results. With half-inch tubes, the lines in the green were clearly and sharply reversed, also some dark lines, not measured, were seen in the blue. The sharpness of these lines depended on the regulation of the hydrogen current, by which the upper stratum of vapour could be cooled at will.

(1) The absorption spectrum of magnesium consists of two sharp lines in the green, of which one, which is broader than the other, and appears to broaden as the temperature increases, coincides in position with the least refrangible of the *b* group, while the other is less refrangible, and has a wave-length very nearly 5210. These lines are the first and the last to be seen, and were at first taken for the extreme lines of the *b* group.

(2) A dark line in the blue, always more or less broad, difficult to measure exactly, but very near the place of the brightest blue line of magnesium. This line was not always visible, indeed rarely when magnesium

alone was placed in the tube. It was better seen when a small quantity of potassium or sodium was added. The measure of the less refrangible edge of this band gave a wave-length of very nearly 4615.

(3) A third line or band in the green rather more refrangible than the *b* group. This is best seen when potassium and magnesium are introduced into the tube, but it may also be seen with sodium and magnesium. The less refrangible edge of this band is sharply defined, and has a wave-length about 5140, and it fades away towards the blue.

These absorptions are all seen both when potassium and sodium are used along with magnesium, and may be fairly ascribed to magnesium, or to magnesium together with hydrogen.

But besides these, other absorptions are seen which appear to be due to mixed vapours.

(4) Thus when sodium and magnesium are used together a dark line, with ill-defined edges, is seen in the green, with a wave-length about 5300. This is the characteristic absorption of the mixed vapours of sodium and magnesium; it is not seen with either vapour separately, nor is it seen when potassium is used instead of sodium.

(5) When potassium and magnesium are used together, a pair of dark lines are seen in the red. The less refrangible of these sometimes broadens into a band with ill-defined edges, and has a mean wave-length of about 6580. The other is always a fine sharp line, with a wave-length about 6475. These lines are as regularly seen with the mixture of potassium and magnesium as the above-mentioned line (5300) is seen with the mixture of sodium and magnesium, but are not seen except with that mixture.

There is a certain resemblance between the absorptions above ascribed to magnesium, and the emission spectrum seen when the sparks of a small induction-coil, without Leyden jar, are taken between electrodes of magnesium.

The coincidences of the series of the solar spectrum hitherto observed have, for the most part, been with lines given by dense electric sparks; while it is not improbable that the conditions of temperature, and the admixtures of vapours in the upper part of the solar atmosphere, may resemble much more nearly those in our tubes.

It became a question of interest to find the conditions under which the same mixtures would give luminous spectra, consisting of the lines which had been seen reversed. On observing sparks from an induction-coil taken between magnesium points in an atmosphere of hydrogen, a bright line regularly appeared, with a wave-length about 5210, in the same position as one of the most conspicuous of the dark lines observed to be produced

by vapour of magnesium with hydrogen in our iron tubes. This line is best seen, *i.e.* is most steady, when no Leyden jar is used, and the rheotome is screwed back, so that it will but just work. It may, however, be seen when the coil is in its ordinary state, and when a small Leyden jar is interposed; but it disappears (except in flashes) when a larger Leyden jar is used, if the hydrogen be at the atmospheric pressure. This line does not usually extend across the whole interval between the electrodes, and is sometimes only seen near the negative electrode. Its presence seems to depend on the temperature, as it is not seen continuously when a large Leyden jar is employed, until the pressure of the hydrogen and its resistance is very much reduced*. When well-dried nitrogen or carbonic oxide is substituted for hydrogen, this line disappears entirely; but if any hydrogen or traces of moisture be present it comes out when the pressure is much reduced. In such cases the hydrogen lines C and F are always visible as well. Sometimes several fine lines appear on the more refrangible side of this line, between it and the *b* group, which give it the appearance of being a narrow band, shaded on that side. Various samples of magnesium used as electrodes, and hydrogens prepared and purified in different ways, gave the same results.

In addition to the above-mentioned line, there is also produced a series of fine lines, commencing close to the most refrangible line of the *b* group, and extending with gradually diminishing intensity towards the blue. These lines are so close to one another, that in a small spectroscope they appear like a broad shaded band. We have little doubt that the dark absorption line, with wave-length about 5140, shading towards the blue, observed in our iron tubes, was a reversal of part of these lines, though the latter extend much further towards the blue than the observed absorption extends.

Charred cream of tartar in iron tubes, arranged as before, gave a broad absorption band extending over the space from about wave-length 5700 to 5775, and in some cases still wider, with edges ill-defined, especially the more refrangible edge. By placing the charred cream of tartar in the tube before it was introduced into the furnace, and watching the increase of light as the tube got hot, this band was at first seen bright on a less bright background, it gradually faded, and then came out again reversed, and remained so. No very high temperature was required for this, but a rise of temperature had the effect of widening the band. Besides this absorption, there appeared a very indefinite faint absorption in the red, with the centre at a wave-length of about 6100, and a dark band, with a tolerably well-defined edge on the less refrangible side, at about a wave-length of 4850, shading away towards the violet. A fainter dark band was sometimes seen

* With greater dispersion this line is seen as the sharp edge of a series of very fine lines shading off towards the blue like the ordinary hydrocarbon spectrum.

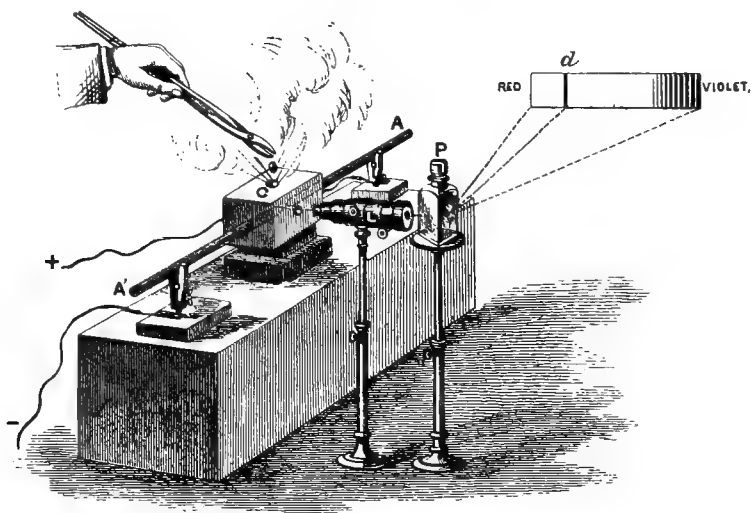
beyond, with a wave-length of about 4645; but sometimes the light seemed abruptly terminated at about wave-length 4850. It will be noticed that these absorptions are not the same as those seen when potassium is heated in hydrogen, nor do they correspond with known emission lines of potassium, although the first, which is also the most conspicuous and regularly visible of these absorptions, is very near a group of three bright lines of potassium. It seemed probable that they might be due to a combination of potassium with carbonic oxide. Potassium heated in carbonic oxide in glass tubes, united readily with the gas, but the compound did not appear to volatilize at a dull red heat, and no absorption, not even that which potassium gives when heated in nitrogen under similar circumstances, could be seen. Induction sparks between an electrode of potassium and one of platinum in an atmosphere of carbonic oxide, gave the usual bright lines of potassium, and also a bright band, identical in position with the above-mentioned band, between wave-lengths about 5700 and 5775. This band could not be seen when hydrogen was substituted for carbonic oxide. A mixture of sodium carbonate and charred sugar, heated in an iron tube, gave only the same absorption as sodium in hydrogen. There were also no indications of any absorption due to a compound of rubidium or of caesium with carbonic oxide.

A mixture of barium carbonate, aluminium filings, and lamp-black, heated in a porcelain tube, gave two absorption lines in the green, corresponding in position to bright lines seen when sparks are taken from a solution of barium chloride, at wave-lengths 5242 and 5136, marked α and β by Lecoq de Boisbaudran. These two absorptions were very persistent, and were produced on several occasions. A third absorption line, corresponding to line δ of Boisbaudran, was sometimes seen; and on one occasion, when the temperature was as high as could be obtained in the furnace fed with Welsh coal, and a mixture of charred barium tartrate with aluminium was used, a fourth dark line was seen with wave-length 5535. This line was very fine and sharply defined, whereas the other three lines were ill-defined at the edges; it is, moreover, the only one of the four which corresponds to a bright line of metallic barium.

Repeated experiments with charred tartrates of calcium and of strontium mixed with aluminium gave no results; but on one occasion, when sodium carbonate was used along with the charred tartrate of strontium and aluminium, the blue line of strontium was seen reversed: and on another occasion, when a mixture of charred potassium, calcium, and strontium tartrates, and aluminium was used, the calcium line, with wave-length 4226, was seen reversed.

In order to command higher temperatures, experiments were made with the electric arc enclosed in lime, magnesia, or carbon crucibles. The different

forms used are represented in the figures on pages 23, 25 and 35 above; and the plan for projecting reversals in the figure hereunder.



In the first experiments thirty cells of Grove were employed; in the later the Siemens arc from the powerful dynamo-machine belonging to the Royal Institution.

The electric arc in lime crucibles gives a very brilliant spectrum of bright lines, a copious stream of vapours ascending the tube. On drawing apart the poles, which could be done for nearly an inch without stopping the current, the calcium line with wave-length 4226 almost always appears more or less expanded with a dark line in the middle, both in the lime crucibles and in carbon crucibles into which some lime has been introduced; the remaining bright lines of calcium are also frequently seen in the like condition, but sometimes the dark line appears in the middle of K (the more refrangible of Fraunhofer's lines H), when there is none in the middle of H. On throwing some aluminium filings into the crucible, the line 4226 appears as a broad dark band, and both H and K, as well as the two aluminium lines between them, appear for a second as dark bands on a continuous background. Soon they appear as bright bands with dark middles; gradually the dark line disappears from H, and afterwards from K, while the aluminium lines remain with dark middles for a long time. When a mixture of lime and potassium carbonate was introduced into a carbon crucible, the group of three lines with wave-lengths 4425, 4434, and 4454 were all reversed, the least refrangible being the most strongly reversed, and remaining so longest, while the most refrangible was least strongly reversed, and for the shortest time.

When aluminium was put into the crucible, only the two lines of that metal between H and K were seen reversed. The lines at the red end remained steadily bright.

When magnesium was put into a lime crucible, the *b* group expanded a little without appearing reversed, but when some aluminium was added, the least refrangible of the three lines appeared with a dark middle, and on adding more magnesium the second line put on the same appearance; and lastly, the most refrangible was reversed in like manner. The least refrangible of the three remained reversed for some time; and the order of reversibility of the group is that of refrangibility inverted. Of the other magnesium lines, that in the yellowish-green (wave-length 5527) was much expanded, while the blue line (wave-length 4703), and a line still more refrangible than the hitherto recorded lines, with wave-length 4354, were still more expanded each time that magnesium was added.

The following experiments were made in carbon crucibles:—

With strontia the lines with wave-lengths 4607, 4215 and 4079 were all seen with dark lines in the middle, but no reversal of any strontium line less refrangible could be seen.

A mixture of barium and potassium carbonates produced the reversal of the lines with wave-lengths 5535 and 4933. When barium chlorate was dropped into a crucible, the four lines with wave-lengths 4553, 4933, 5545, and 5518 were reversed.

To observe particularly the effects of potassium a mixture of lime and potassium carbonate previously ignited was thrown in. The violet lines of potassium, wave-length 4044, came out immediately as a broad black band, which soon resolved into *two* narrower dark bands having wave-lengths nearly 4042 and 4045. On turning to the red end the two extreme red lines were both seen reversed. No lines of potassium between the two extremes could be seen reversed, but the group of three yellow lines were all expanded, though not nebulous, and other lines in the green were seen much expanded.

Sodium carbonate gave only the D lines reversed, though the other lines were expanded, and the pairs in the green had each become a very broad nebulous band, and D almost as broad a black band. When sodium chlorate was dropped into a crucible, the pair of lines, with wave-lengths 5681, 5687, were both momentarily reversed, the latter much more strongly than the former.

When a very little charred rubidium tartrate was put in, the two violet lines were sharply reversed, appearing only as black lines on a continuous light background. Turning to the red end, the more refrangible of the two lines in the extreme red (wave-length 7800) was seen to have a decided dark

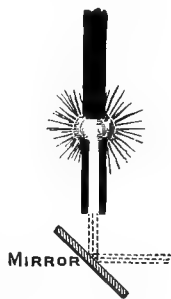
line in the middle, and it continued so for some time. The addition of more rubidium failed to cause any reversal of the extreme red line, or of any but the three lines already mentioned.

On putting lithium carbonate into the crucible, the violet line of lithium appeared as a nebulous band, and on adding some aluminium this violet band became enormously expanded, but shewed no reversal. The blue lithium line (wave-length 4604) was well reversed, as was also the red line, while a fine dark line passed through the middle of the orange line. On adding a mixture of aluminium filings and the carbonates of lithium and potassium, the red line became a broad black band, and the orange line was well reversed. The green line was exceedingly bright, but not nebulous or reversed, and the violet line still remained much expanded, but unreversed.

Metallic indium placed in the crucible gave the lines with wave-lengths 4101 and 4509, and both were seen strongly reversed. No other absorption line of indium could be detected.

In some cases a current of hydrogen, or of coal-gas, was introduced into the crucibles by means of a small lateral opening, or by a perforation through one of the carbon electrodes, as is shewn in the figure on page 35; sometimes the perforated carbon was placed vertically, and we examined the light through the perforations as in the figure. When no such current of gas is introduced, there is frequently a flame of carbonic oxide burning at the mouth of the tube. The current of hydrogen produces very marked effects. As a rule, it increases the brilliance of the continuous spectrum, and diminishes relatively the apparent intensity of the bright lines, or makes them altogether disappear with the exception of the carbon lines. When this last is the case, the reversed lines are seen simply as black lines on a continuous background. The calcium line with wave-length 4226 is always seen under these circumstances as a more or less broad black band on a continuous background, and when the temperature of the crucible has risen sufficiently, the lines with wave-lengths 4434 and 4454, and next that with wave-length 4425, appear as simple black lines. So, too, do the blue and red lines of lithium, and the barium line of wave-length 5535, appear steadily as sharp black lines, when no trace of the other lines of these metals, either dark or bright, can be detected. Dark bands also frequently appear, with ill-defined edges, in the positions of the well-known bright green and orange bands of lime.

With sodium chloride, the pair of lines (5687, 5681) next more refrangible than the D group were repeatedly reversed. In every case the less refrangible of the two was the first to be seen reversed, and was the more



strongly reversed, as has also been observed by Mr Lockyer. But our observations on this pair of lines differ from his in so far as he says that "the double green line of sodium shews scarcely any trace of absorption when the lines are visible," while we have repeatedly seen the reversal as dark lines appearing on the expanded bright lines; a second pair of faint bright lines, like ghosts of the first, usually coming out at the same time on the more refrangible side.

Potassium carbonate gave, besides the violet and red lines which had been reversed before, the group, wave-lengths 5831, 5802, and 5872, all reversed, the middle line of the three being the first to shew reversal. Also the lines wave-lengths 6913, 6946, well reversed, the less refrangible remaining reversed the longer. Also the group, wave-lengths 5353, 5338, 5319, reversed, the most refrangible not being reversed until after the others. Also the line wave-length 5112 reversed, while two other lines of this group, wave-lengths 5095 and 5081, were not seen reversed.

Using lithium chloride, not only were the red and blue lines, as usual, easily reversed, and the orange line well reversed for a long time, but also the green line was distinctly reversed; the violet line still unreversed, though broad and expanded. Had this green line belonged to cæsium, the two blue lines of that metal which are so easily reversed could not have failed to appear; but there was no trace of them.

In the case of rubidium, the less refrangible of the red lines was well reversed as a black line on a continuous background, but it is not easy to get, even from the arc in one of our crucibles, sufficient light in the low red to shew the reversal of the extreme ray of this metal.

With charred barium tartrate, and also with baryta and aluminium together, the reversal of the line with wave-length 6496 was observed, in addition to the reversals previously described. The less refrangible line, wave-length 6677, was not reversed.

With charred strontium tartrate, the lines with wave-lengths 4812, 4831, and 4873 were reversed, and by the addition of aluminium, the line wave-length 4962 was reversed for a long time, and also the lines wave-lengths 4895, 4868.

On putting calcium chloride into the crucible, the line wave-length 4302 was reversed, this being the only one of the well-marked group to which it belongs which appeared reversed. On another occasion, when charred strontium tartrate was used, the line wave-length 4877 was seen reversed, as well as the strontium line near it. The lines wave-lengths 6161, 6121 have been seen momentarily reversed.

With magnesium, when a stream of hydrogen or of coal-gas was led into the crucible, the line wave-length 5210, previously seen in iron tubes, and

ascribed to a combination of magnesium with hydrogen, was regularly seen, usually as a dark line, sometimes with a tail of fine dark lines on the more refrangible side similar to the tail of bright lines seen in the sparks taken in hydrogen between magnesium points. Sometimes, however, this line (5210) was seen bright. It always disappeared when the gas was discontinued, and appeared again sharply on readmitting hydrogen. These effects were, however, only well-defined in crucibles having a height of at least 3 inches above the arc.

On putting a fragment of metallic gallium into a crucible, the less refrangible line, wave-length 4170, came out bright, and soon a dark line appeared in the middle of it. The other line, wave-length 4031, shewed the same effect, but less strongly.

Reviewing the series of reversals which have been observed, in many cases the least refrangible of binary groups is the most easily reversed, as has been previously remarked by Cornu.

Making a general summation of the results respecting the alkaline earth metals, potassium and sodium, having regard only to the most characteristic rays, which for barium may be taken as 21, for strontium 34, for calcium 37, for potassium 31, and for sodium 12, the reversals number respectively 6, 10, 11, 13, and 4. That is in the case of the alkaline earth metals about one-third, and these chiefly in the more refrangible third of the visible spectrum, the characteristic rays remaining unreversed in the more refrangible part of the spectrum being respectively 2, 5, and 4.

The curious behaviour of the lines of different spectra with regard to reversal induced a comparison with the bright lines of the chromosphere of the sun, as observed by Young. It is well known that some of the principal lines of the metals giving comparatively simple spectra, such as lithium, aluminium, strontium, and potassium, are not represented amongst the dark lines of Fraunhofer, while other lines of those metals are seen: and an examination of the bright chromospheric lines shews that special rays highly characteristic of bodies which, from other rays, appear to be present in the chromosphere, are absent, or are less frequent in their occurrence than others.

In the table on pages 30 and 31 above, the relation between the observations on reversals and Young's on the chromospheric lines is shewn.

The group calcium, barium, and strontium on the one hand, and sodium, lithium, magnesium, and hydrogen, on the other, seem to behave in a similar way in the chromosphere of the sun; but before definite conclusions can be reached regarding the sequence of the reversals, a further series of long and laborious experiments must be executed.

ON THE REVERSAL OF THE LINES OF METALLIC VAPOURS

[*Proceedings of the Royal Society*, Vol. xxix. (1879), pp. 402 sqq.]

THE experiments of which the results are here given were all made in the Chemical Laboratory of the Royal Institution, with the powerful electric current from the Siemens dynamo-electric machine. Limestone crucibles similar to those before employed were in all cases used, but the opening through which the arc was observed was in general placed horizontally, so that the axis of the collimator of the spectroscope was directed immediately on to the arc without the intervention of a mirror, and a small vertical opening was made for the introduction of the substances under observation, and was closed when not in use by a piece of lime.

With sodium carbonate the green pair wave-lengths 4983, 4982 were reversed, shewing dark lines in the middle of the bright ones, the less refrangible of the two giving the stronger dark line. The sodium line given by Lecoq de Boisbaudran at wave-length 4670 shewed as a diffuse blue band with a *pair* of fine dark lines in it, of which the stronger and more lasting was the less refrangible. The diffuse blue band resolved itself into *two* diffuse lines as the sodium carbonate evaporated, and the measurement of their positions in comparison with a conspicuous titanium line, which lies between them, and was made to shew at the same time by introducing a fragment of titanic oxide into the crucible, gave for this sodium pair the wave-lengths 4667, 4664. The orange pair, wave-lengths 6160, 6154, were also seen reversed in like manner, but we failed to detect any difference in the strength or continuance of the dark lines in this case. These reversals of sodium lines were many times observed, and we noticed that the reversals of the other pairs continued after that of the red pair had ceased to be visible, that next after the disappearance of the dark lines in the red pair those in the diffuse blue pair ceased to be visible, then the dark lines in the green pair, and then those in the yellowish-green (5687, 5681). In some cases when a large quantity of sodium carbonate was put into the crucible a curious double reversal occurred. In the middle of an enormous dark expansion of D a bright yellow band appeared, which in turn had a narrower dark band, or a pair of dark lines, in its middle. A similar

double reversal of the lithium blue line occurred so far as to shew a bright line in the middle of the dark one. Of the two violet lines of potassium we observed that the more refrangible remained reversed longer than the other.

In addition to the reversals of calcium lines before observed by us, we have noticed the reversal of all the more conspicuous calcium lines of the G group, viz., those wave-lengths—4282, 4289, 4298, 4307, 4318, besides 4302 before noted, also that of 4379, and all three lines of a triplet 4585, 4581, 4578. The finer lines, wave-lengths 4434·3, 4454·5, slightly less refrangible than the strong lines 4434, 4454, were reversed, but only when one of the poles was a bar of iron, instead of carbon. The strong lines just mentioned were expanded so as to cover their neighbours, and all four lines were seen black against the bright background in the positions and of the same relative strengths as when bright.

When strontium chloride was put into the crucible the lines with the following wave-lengths, besides those before noted, were observed reversed—4305, 4865, 4892, 5223, 5225, 5228, 5480, 5503, 5522, and momentarily only, 5155, 5238, 5256. Besides these, many dark bands were observed in the less refrangible part of the spectrum, of which three, with wave-lengths 5920, 6035, 6060, appear to be identical with bright bands ascribed to strontia, and one, with wave-length 6597, is identical with a bright line given by strontium chloride.

Manganese, introduced as sulphate, gave with facility the violet triplet 4029, 4032, 4033 as dark lines on the continuous background. The bright blue lines of manganese were not, however, reversed until some metallic magnesium was introduced. This brought out the reversal of the lines, wave-lengths 4753, 4783, and 4823, the last being the most easily reversed of the three.

Lead introduced in the metallic state gave a reversal of the violet line, wave-length 4058, which Cornu had previously seen reversed, but this reversal was far better seen, becoming a wide black band, when the lead was introduced as an alloy with zinc. Probably the lead vapour was not so rapidly oxidised when mixed with zinc, and a thicker, if less dense, stratum interposed between the arc and the spectroscop. When lead ferrocyanide was used, not only the line above-mentioned was reversed, but also much less strongly, a line near it, wave-length 4062.

With zinc, only the less refrangible two of the three blue lines, wave-lengths 4810, 4721, were seen reversed. The very bright lines, wave-lengths 4924, 4911, seen in the spark between zinc poles, were not seen by us at all in the arc, resembling in this respect the magnesium line, wave-length 4481, and the cadmium lines, wave-lengths 5377, 5336.

When cadmium was put into the crucible the lines, wave-lengths 5085, 4799, and 4677, were reversed, not the line, wave-length 4415. With

a large dose of cadmium the red line, wave-length 6438, was once seen reversed for an instant only.

With silver, besides the reversals before observed by us, the line, wave-length 4053, shewed a dark line in the middle of its expansion as noticed by Mr Lockyer, but we could see no reversal of the line, wave-length 4208. Instead of the reversal of this line we observed that a second bright line came out close to it, rather diffuse, and about midway between the line 4208 and the calcium line 4215. By measuring the intervals and interpolating, we deduced 4211·3 for the wave-length of this silver line, which we could see, though it was fainter, in the less powerful current of a De Meritens' machine. This second line coming out near the other silver line gave the appearance of a reversal in the middle of a diffuse line, but besides the measurements made with a micrometer we assured ourselves of the fact of there being two lines by watching the fading of the second line as the silver evaporated. The use of an alloy of zinc with silver did not alter the appearance of these two lines, or bring out a reversal of either of them. We failed to see any line of silver either bright or reversed with wave-length about 4240, as mentioned by Cornu, whether the silver were used pure or alloyed with zinc or with lead. With the carbons arranged vertically as shewn in our last communication on this subject (p. 35 above), and the light viewed through the perforated carbon, silver gave a channelled spectrum as described by Lockyer and Roberts. As this channelled spectrum was not seen with silver in any other arrangement of our crucibles, we are led to attribute it to a comparatively cool condition of the silver vapour ascending the carbon tube, a condition of near approach to a state of liquefaction.

Having observed that lines frequently came out with mixtures which were not visible when the separate ingredients were used, we tried a few amalgams. None of these shewed any reversals of the mercury lines. But an amalgam of bismuth gave readily the reversal of the bismuth line, wave-length 4722, and with more difficulty that of the line, wave-length 4119.

Antimony did not appear to give any lines, or none easily distinguishable, in the arc.

With copper we observed the reversal of two lines only, wave-lengths 5105, 5153.

Iron introduced as metal, or as chloride, in the usual way, gave us no reversal; with an iron rod used as positive pole instead of one of the carbons, we succeeded in getting the reversal of one line, wave-length 4045, which expanded and shewed a fine dark line in its middle; but by passing an iron wire into the arc through the positive carbon, which was perforated in the manner described in our last communication on this subject (p. 35), for the introduction of gases into the arc, and pushing in the wire slowly as the end

burned away, we succeeded in reversing several of the brightest of the iron lines. The three violet lines, wave-lengths 4045, 4063, 4071, were the first to be reversed. They all expanded before shewing reversal, and the order of reversal was that of refrangibility. Besides these the lines, wave-lengths 4957, 4920 (the stronger and less refrangible of a pair), 4404, 4383, 4325, 5040, 4307 (G), were reversed. These last two lines could not be certainly distinguished from calcium lines, as the last is almost if not quite coincident with a calcium line, and the other is too close to a calcium line to be distinguished without more exact measurement than the time during which it could be observed would allow, but we judged from their relative intensity that they were the iron lines. The line, wave-length 4415, was not seen reversed when the other bright lines near it were reversed.

Nickel, whether put into the crucible in the old way, or fed into the arc in small fragments filling a platinum tube which was passed through a perforated carbon pole, gave no definite reversal of any of its lines; nor did cobalt, even when a bar of cobalt was used as the positive pole.

Tin, palladium, and platinum gave no reversals.

It is worthy of remark in regard to the difficulty of obtaining substances chemically pure, that we found that carbon poles which had been for some hours ignited in a current of chlorine and further intensely heated in the arc, while chlorine was passed through perforations down their axes, still shewed in the arc, of course without any crucible being employed, a multitude of lines, amongst which the so-called carbon lines and those of calcium and iron were conspicuous.

ON THE SPECTRA OF SODIUM AND POTASSIUM

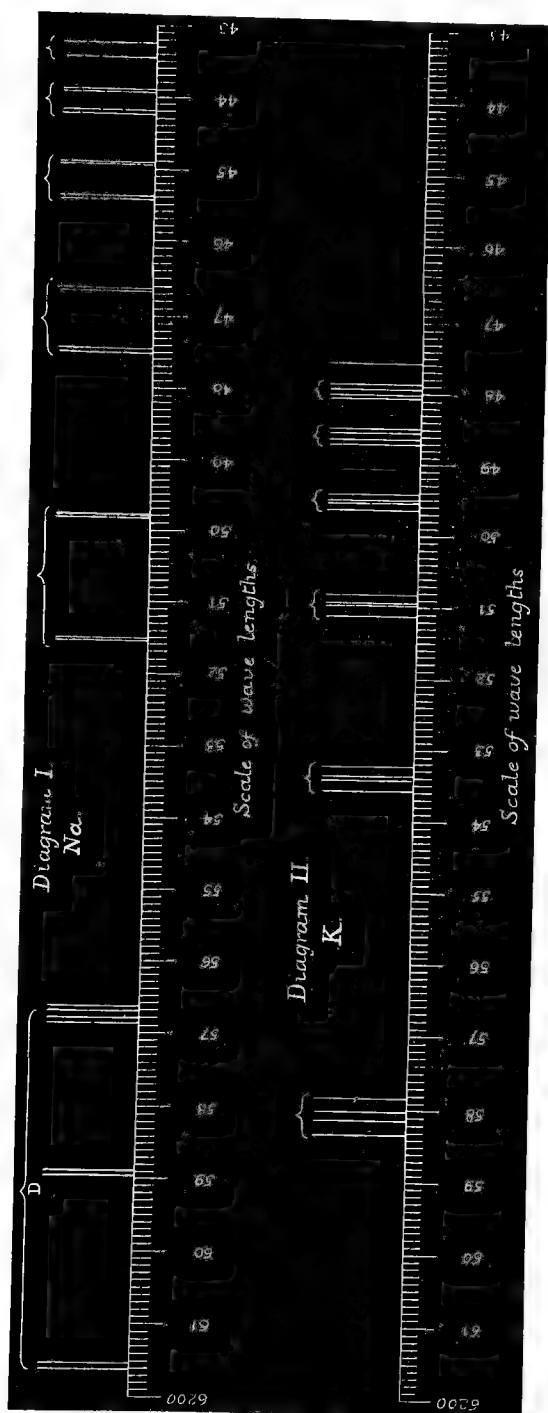
[*Proceedings of the Royal Society*, Vol. XXIX. (1879), pp. 398 sqq.]

IN the course of our observations on the reversal of the spectra of metals, we have many times had occasion to observe the spectra of sodium and potassium, and have noticed that they have been imperfectly described. M. Lecoq de Boisbaudran describes them more completely than anyone else; but as seen in the electric arc in one of the crucibles described by us in connexion with the reversals, there are in each spectrum several additional lines, which make the whole far more regular and symmetrical than they appear in his account. These additional lines are seen in the arc given by a battery of 25 Grove's cells as well as in that given by a dynamo-electric machine. They shew best in a long arc, and as the vapours conduct well it is easy to draw out the arc of 25 cells to the length of an inch or more. We have generally used carbonates of the metals, sometimes chlorides.

In the case of sodium we have already noticed (p. 35 above, last three lines) that the pair of lines next more refrangible than D (which we may for convenience call the third group) are accompanied by a fainter pair on their more refrangible side. Lecoq de Boisbaudran notices one only of these faint lines. By micrometer measurements of their distances from their brighter companions, we have deduced the wave-lengths 5673·6, 5668·6, for this pair. A line closely corresponding to the latter of these lines is to be found in Kirchhoff's map of the Solar Spectrum (1165·2).

The next pair of lines, or fourth group (5155, 5152), are sharply defined, and have no other line close to them; but the bright green pair, or fifth group (4983, 4982), are diffuse lines, usually seen as a band but noted by Lockyer to be a double line, and have a third line on their more refrangible side, of which we find the wave-length to be 4980·5. We feel sure that there ought to be a fourth line in this group, but have never been able to detect it. It is possible that two of the four lines may overlap, and so appear as one; but the reversal of the brighter pair of the group seems to militate against such a supposition, as the third line has not been seen reversed. It is, however, much fainter than the other two.

Spectrum of Sodium in the arc in a lime crucible.



Spectrum of Potassium in the arc in a lime crucible, exclusive of red and violet lines.

The sixth group consists of a pair of lines sharply defined, for which we have found, by measurements of their distances from some bright manganese lines in their neighbourhood, the wave-lengths 4751·4, 4747·5. The first only of this pair is described by Lecoq de Boisbaudran. We have not seen either of them reversed, but there are lines in the solar spectrum which correspond closely to them and may therefore reasonably be attributed to sodium.

The seventh group is a pair of lines with diffuse edges, which we have seen reversed as fine dark lines in the middle of the diffuse blue bands. For these we deduced the wave-lengths 4667·2, 4663·7. The first only is described by Lecoq de Boisbaudran, and he assigns to it the wave-length 4670. By putting some titanite oxide into the crucible the titanium line 4666·5 was seen between the sodium lines, and we have no doubt that it is sodium which gives the winged appearance to the corresponding ray in the solar spectrum. The ray 4663·5 in the "normal solar spectrum" is probably the other ray of this pair, as the difference between the wave-length of this and that found by us is within the limits of error in our measurements of such diffuse lines.

The eighth group is a more sharply defined pair, for which by measurement of their distances from neighbouring barium lines we deduced the wave-lengths 4543·6, 4540·7. The lines 4543·9, 4540·2 in the "normal solar spectrum" probably represent this pair.

The ninth group is again a diffuse pair for which we deduced, by measurements from two bright manganese lines near them, the wave-lengths 4496·4, 4494·5. These are too diffuse for very exact measurement, but a bright line, which we could not certainly recognise as the manganese line 4495, appears nearly coincident with the more refrangible of them. Lines nearly corresponding to these are in the solar spectrum.

The tenth group is again a more sharply defined pair, for which, by measurements from calcium and iron lines, we found the wave-lengths 4423, 4419·5. The lines 2656·7, 2664·9 of Kirchhoff's map of the solar spectrum may represent this pair.

The eleventh group is a very diffuse pair, sometimes seen as a continuous band dividing as the sodium evaporates, for which we found the wave-lengths about 4393, 4390. There is a line corresponding to the former in the "normal solar spectrum," and Kirchhoff's line 2709·6 may represent the latter.

The twelfth group is a diffuse but narrow band, which we have not seen divided. The middle of it has a wave-length about 4343, very nearly coincident with a line which we took to be an iron line, and rather more refrangible than a chromium line 4344·5.

The thirteenth group is a diffuse broad band nearly bisected by the iron line 4325.

The successive groups become fainter and more diffuse as they are more refrangible, at the same time the distance between successive groups diminishes. Their positions are shewn on the accompanying diagram to a scale of wave-lengths. It is worthy of note that every alternate group is much more sharply defined than the others. Moreover, it is only the diffuse groups (3), (5), (7) which shew reversal except the first group, in the orange, which, however, is more difficult of reversal than the others. The whole series, exclusive of D, looks very like repetitions of the same set of vibrations in a harmonic progression; the first (visible) term consisting of the six vibrations represented by the orange pair (6160, 6154) and the four lines of group (3); the next term of the five lines of the fourth and fifth groups, one of the six vibrations being now too faint to be seen; the next three terms, of each of which only four lines are visible, consisting of the sixth and seventh, and eighth and ninth, and the tenth and eleventh groups, and the last term of the two faint bands of the twelfth and thirteenth groups.

Simple harmonic relations can be found to subsist between some of the groups; for instance, the wave-lengths of the fifth, seventh, and eleventh groups are very nearly as $\frac{1}{15} : \frac{1}{16} : \frac{1}{17}$, but the whole series cannot be represented as simple harmonics of one set of six vibrations with any probability. The smallest numbers, which are nearly proportional to the reciprocals of the wave-lengths of groups (1), (4), (6), (8), (10), (12), are 81, 97, 105, 110, 113, 115; and these numbers are only approximately in the same ratios as the reciprocals of wave-lengths.

The potassium spectrum as seen in the arc, leaving out of account the two pairs of lines in the red and that in the violet, consists of a series of groups of four lines each, succeeding one another at shorter intervals and becoming fainter as they are more refrangible. They all are more or less diffuse, markedly more so on their less refrangible edges. They are shewn on the accompanying diagram to a scale of wave-lengths. Lecoq de Boisbaudran gives a more complete list of potassium lines than other observers, but while the spark which he used brought out several lines which are not seen in the arc, the higher terms of the rhythmical series brought out very distinctly by the arc are not so well seen in the spark.

The first and least refrangible group of this series consists of the four lines to which Lecoq de Boisbaudran assigns the wave-lengths 5831, 5812, 5801, 5783. The second of these lines (5812) is much less strong than the others as seen in the spark. In the arc they are all nearly equal in brightness, but we have not seen the second line reversed.

Between the first and second group Lecoq de Boisbaudran gives a line which was not noticed by us in the arc.

In the second group the two middle lines are very close, and Lecoq de Boisbaudran gives only their mean wave-length. Measuring the distances of the middle from the extreme lines of the group, the wave-lengths of this quartet are 5355, 5338, 5334.5, 5319. These are all about of equal brightness, but we have not seen the third (5334.5) reversed.

The third group consists of the lines 5112, 5098, 5095, 5081. Of these the second is not given by Lecoq de Boisbaudran, and only the first has been seen by us reversed.

Three lines given by Lecoq de Boisbaudran between the third and fourth groups are not seen in the arc, or at least are not nearly so conspicuous as the groups here described.

The fourth group consists of lines for which we find the wave-lengths about 4964, 4956, 4950, 4942. Of these the first and last only are given by Lecoq de Boisbaudran as 4963 and 4936.

The fifth group has lines of which we find the wave-lengths about 4870, 4863, 4856, 4850.

The sixth group has lines of about the wave-lengths 4808, 4803, 4796, 4788.

The seventh group is too faint and diffuse to be distinctly resolved. The wave-length of the least refrangible edge is about 4759.

None of these last three groups are seen by Lecoq de Boisbaudran, and they are too diffuse for exact measurement; on the other hand, he gives several other lines which are not noticed by us in the arc.

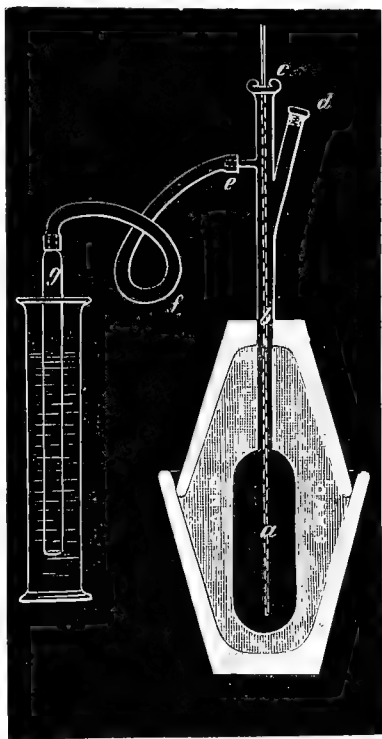
As in the case of sodium the repetition of these quartets of lines at decreasing intervals with decreasing brightness and sharpness as they proceed from the less to the more refrangible, gives the impression of a series of harmonics; but the wave-lengths do not seem to be in a simple harmonic progression, though simple harmonic relations may be found between some of the groups.

QUANTITATIVE SPECTROSCOPIC EXPERIMENTS

[*Proceedings of the Royal Society*, Vol. XXIX. (1879), pp. 482 sqq.]

THE well-known expansion of the lines of sodium and other metals, when increased quantities of the metals are introduced into the flame or arc, seems to afford a means of attaining a quantitative spectrum analysis in certain cases, if the relations between the width of the lines and the thickness, density, and temperature of the vapours could be determined. We had such a determination in view during our experiments on the reversal of the lines of metallic vapours heated in iron tubes, and have since made a good many experiments expressly for the purpose. We have not yet overcome all the difficulties attending these experiments; nevertheless, some results, definite and interesting, have been reached, which we now communicate to the Society.

The first experiments were made with wrought iron bottles, of the form shewn in the accompanying figure. To prevent the diffusion of carbonic oxide from the fire we found it essential to have the wide part, *a*, and part of the tube, *b*, coated with borax. The bottle was then packed in sand in two crucibles, one of them inverted, and heated in a small furnace fed with gas retort carbon. The bottle was previously treated with fused caustic potash at a red heat, and washed with acid. Any oxide remaining in the bottle was reduced by a current of hydrogen introduced by the side tube *e*, and forced to pass to the bottom by allowing it no exit except by a narrow tube passed through the opening *c* and reaching nearly to the bottom of the



bottle, as shewn by the dotted lines. The hydrogen was then replaced by nitrogen, the narrow tube removed, *c* closed by a glass plate through which the spectrum was viewed, and the side tube *e* connected by a thick rubber tube with a glass tube for collecting the gas driven out by the metallic vapour, or with a manometer formed of an inverted burette dipping into a vessel of water. The sodium, weighed in dry carbonic acid gas, was introduced in little iron cups about the size of gun caps through the oblique side tube *d*, and the orifice instantly closed with a rubber stopper, for the purpose of measuring the gas expelled as the sodium evaporated. This orifice was fitted with a screw cap, for use when the pressure of the gas in the bottle was to be varied.

Attempts to measure the temperature of our furnace were not very successful. Observations of temperature depending on the electromotive force of a thermo-electric junction of platinum and palladium, which had been carefully calibrated in boiling mercury, boiling cadmium, and boiling zinc, failed at the temperature at which our experiments were made from the fusion of the palladium. This indicates, from Violle's experiments, that the temperature of the furnace was about 1500°C .

The bottles, however carefully cleaned, were never quite free from sodium, so that on observing, at first, the spectrum emitted by the hot bottom of the bottle, the D absorption was seen as two fine lines.

On introducing a fragment of sodium (.015 or .020 grm.) the following phenomena were observed with the spectroscope. First D appeared as a narrow *bright* band, considerably brighter than the general spectrum of the bottle, with the fine pair of dark lines quite unexpanded in its midst; this bright band rapidly expanded, becoming fainter and more diffuse as it expanded, was visible to a width equal to fourteen or sixteen times the distance of the D lines from each other, and then died away entirely, leaving the fine dark lines much as they were at first. The addition of several pieces of sodium in succession produced a repetition of the same phenomena, the D absorption lines being but very little wider after the introduction of sodium enough to fill the bottle with its vapour.

Larger pieces of sodium produced an increased width of expansion of the bright band; but from the very diffuse character of the edges of the band and from its being seen against a background only a little less bright, it was not possible to get any exact measures of the widths to which the bands expanded.

On observing the gas expelled from the bottle, it was found that the expansion of the bright band was synchronous with the expulsion of gas, and ceased when gas ceased to come out; that is to say, it was synchronous with the expansion of the sodium vapour within the bottle. It was found, however, that when the gas ceased to be expelled from the bottle, it almost

immediately began to be sucked back, and that nearly, if not quite, as rapidly as it had been expelled, until not only the whole gas expelled was drawn in again, but generally a small quantity of nitrogen in addition. In a few seconds, not only had the sodium vapour ceased to have any sensible tension, but a portion of the nitrogen (2 to 3 cub. centims.) had been absorbed. There was no absorption of nitrogen before the sodium was put in, and when the equilibrium had been attained, which was always in less than a minute, there was no absorption afterwards.

These phenomena seemed to indicate, (1), either that the temperature of the sodium vapour was higher than that of the iron, or that the emissive power of sodium vapour for light of the wave-length of D was greater than that of iron at the temperature of the furnace; (2), that the width of the bright D line, or band, increased with the depth of the stratum of sodium when the density was not increased, inasmuch as the pressure to which the sodium vapour was subject was always the same, and the only, or the principal, change during the expansion of the sodium vapour in the bottle was in the thickness of the layer of vapour; (3), that iron either has the power of forming a compound with sodium, which is very stable at the temperature of the furnace, or else it has a power of transmitting sodium vapour analogous to that which platinum has in regard to hydrogen. This last supposition seems to be negatived by the fact that we found that out of .220 gm. of sodium put into the bottle in a series of experiments on one occasion, .198 gm. was afterwards extracted when the bottle was cold by washing it out with hydrochloric acid. The effect was not due to the nitrogen, since the sodium appeared to be taken up in the same way when carbonic oxide was substituted for nitrogen.

This behaviour of iron towards sodium explains a phenomenon which had puzzled us when operating before with iron tubes, viz., that it required a very large quantity of sodium, many times the normal amount, to fill one of the tubes with sodium vapour. It also seems to explain the fact observed by Mr Lockyer (*Proc. Roy. Soc.*, Vol. xxii, p. 371), that sodium heated in a long iron tube gives the D absorption line "no thicker than when seen under similar conditions in a test tube."

We came, of course, to the conclusion that it was useless to pursue the investigation of the quantitative measure of sodium vapour by experiments in iron vessels; and we had a stout platinum tube made, half an inch in diameter and 23 inches long, connected by a union joint with an iron tube with fittings similar to those of the top of the iron bottles before described; and also a bottle similar to the iron bottles, but entirely of platinum. When used, the tube was packed with magnesia inside a wider porcelain tube, and the bottle was packed with lime in blacklead crucibles.

For convenience in introducing the sodium, a fine platinum tube, about 1 millim. in diameter, was filled with sodium by sucking up the melted metal, and different lengths of this tube were cut off as required, wrapped at once in thin platinum foil, and dropped into the heated vessel. Amalgams containing various percentages of sodium were also employed. In the case of amalgams containing 1 per cent. and upwards the pieces were weighed; those containing less than 1 per cent. were measured by a very fine pipette. In all cases the amalgam was introduced into the hot vessel wrapped in platinum foil.

For varying the pressure within the vessels, and so by compression or expansion varying the density and thickness of the stratum of metallic vapour under observation, an ordinary compressing and exhausting syringe, connected with a gauge, was used. With the bottle we could not venture to reduce the pressure below that of the atmosphere, lest the softened platinum should collapse; but in the case of the tube the pressure could be reduced to one-fourth of an atmosphere. Into both vessels we have pumped nitrogen until the pressure reached three atmospheres.

Whenever it was desired to empty the vessel of sodium, in order to begin a fresh series of experiments without the necessity of cooling the vessel, the sodium (or sodium and mercury) vapours were blown out by a current of hydrogen passed down to the bottom of the vessel in the mode already described, and when the metallic vapours were sufficiently expelled, the hydrogen was replaced by nitrogen. In this way, though the last traces of sodium were never expelled, the D absorption could be reduced to two narrow lines.

On introducing a fragment of sodium into the hot vessel, when free, or nearly so, from sodium to begin with, the *bright* yellow band rapidly expanding and becoming fainter and more diffuse, and finally dying away, was seen as in the iron bottles; but instead of the D absorption remaining narrow as it had been before, it began to increase in width as the bright band died away, and soon attained a maximum width, and remained steadily at that width—a width several times that of the distance between the D lines, but much less than that of the bright band at its widest. A second piece of sodium thrown in produced a repetition of the same phenomena, except that the bright band was obscured by the absorption of the layer of sodium vapour first introduced, and only seen when it expanded beyond the absorption band. More pieces of sodium produced like effects; the absorption band gradually widening as more sodium was put in, until the channelled spectrum began to appear.

The effects of compressing the vapour were very remarkable. As the pressure increased the channelled spectrum speedily disappeared, then the diffuse edges of the D band contracted, the band itself likewise contracting

until it became a very fine pair of lines, or if the amount of sodium present was not too much, D came out bright. On letting off the pressure, the phenomena recurred in the reverse order, and the whole could be repeated several times. After compression as long as the pressure was sustained the D absorption remained permanently narrowed, but did not continue bright. When there was only a very little sodium in the platinum tube and the pressure diminished, the D band was seen to expand and become diffuse, contracting again as the pressure was restored, but not generally contracting to quite the former width or sharpness.

We used sometimes amalgams of sodium in order to have a very dense gas to retard diffusion, and for the purpose of getting various quantities of sodium diffused through equal spaces. With these amalgams the general course of the phenomena was much the same as with the metal alone, except that we could not by compression to three atmospheres make the D lines shew out so bright as with sodium alone, although the absorption was reduced to extremely narrow dimensions.

One set of experiments was made with a series of amalgams containing decreasing percentages, all less than 1 per cent., of sodium; equal quantities of each were put into the hot tube in succession, the vapour of each being blown out before the next was put in. The thickness of the layers observed was thus very nearly constant, but the density of the sodium vapour variable. It was calculated that the mercury vapour would, at the temperature of the tube, fill a height of about 20 centims. The D absorption was very broad, with wide diffuse edges, with an amalgam of $\frac{1}{2}$ per cent., and did not sensibly diminish in width until the percentage of sodium was reduced to $\frac{1}{8}$.

The results of the foregoing experiments may have been complicated by the sodium vapour which diffused into the cool part of the vessel. We have attempted to overcome this complication by passing down into the bottle, when full, or nearly full, of sodium vapour, a platinum tube closed at the top with a glass plate, and filled with nitrogen, and observing the absorption through this tube. The nitrogen in the tube prevents for a short time the entry of the sodium vapour into the tube, and so by passing the tube to different depths, the thickness of the layer of sodium through which the observations were made could be varied. It was found in this way that a layer of sodium vapour, about 4 centims. thick at the atmospheric pressure at the temperature of our furnace, gave the D absorption sharp and very narrow, but as the sodium diffused into the tube the absorption extended until it produced a broad band with diffuse edges. Without a long process of washing, it is impossible to clear the tube of sodium, so that the repetition of observations in this way is a very tedious business. We are looking for some transparent substance which will stand the high temperature and

the action of sodium, wherewith to close the lower end of our tube of inspection. We have tried a plate of colourless sapphire, but it very soon became too opaque for further use. Perhaps fused alumina may do better.

A few experiments made in a similar way with thallium in iron bottles, shewed on the whole similar results. No bright green line was seen on dropping in a piece of thallium, but it was not until after the lapse of some seconds that the absorption line was apparent. It was faint at first, gradually deepening, and soon attaining a maximum of intensity, when it was remarkably stationary for a long time. More pieces of thallium introduced successively produced a small but perceptible widening of the absorption band and a diminution of the sharpness of its edges.

The foregoing account gives the general course of the phenomena, and it seems useless at present to describe further details, because the quantitative results which we hoped to give are for the time in abeyance until we can ascertain more correctly the temperature of our furnace and the thickness of the layer of vapour observed. This requires an accurate knowledge of the density of the vapour, which could not be satisfactorily deduced from the experiments made with iron bottles, as they did not accord well and were complicated by the action of iron on sodium above described. The platinum vessels stand but few experiments without repair, which causes considerable delay; and the above-mentioned results have necessitated the expensive operation of the reconstruction of some five platinum bottles.

The phenomena attending the compression of the vapours, as well as those of the amalgams of varying percentages, seem to indicate that the width of the D absorption is dependent on the thickness and temperature of the absorbent vapour rather than on the whole quantity of sodium present in it. Very minute quantities diffused into the cool part of the tube appear to give a broad diffuse absorption, while a layer of denser vapour of small thickness in the hottest part of the vessel gives but a very narrow absorption. This may, however, be due to the variation of temperature.

The phenomena of the bright D band seen on compressing the vapour is due to the elevation of temperature consequent on compression. This elevation, we have calculated, for a *sudden* compression to half the original volume, will amount in the case of sodium vapour, if the ratio of the specific heat at constant pressure to that at constant volume be taken as 1.14, to about one-third of the original temperature, whatever that temperature be; so that, allowing for loss during slower compression, the temperature of the vapour in our bottles will have nearly reached 2000° C. In the case of the amalgams the main portion of the gas being mercury vapour, the effect of compression to a like amount will increase the temperature by nearly

two-thirds, in consequence of the ratio of the specific heat at constant pressure to that at constant volume being now 1.66. It is not so easy to explain why the bright band should appear while the sodium is evaporating, when a depression of temperature should ensue. The depression of temperature will, however, affect the hot bottom of the vessel, and so it and the lowest layer of sodium vapour may be relatively cooler than the layers above. Professor Stokes has suggested another cause which may intensify the effect, depending on the fact that the radiation from the sides of the vessel is partly reflective, partly emissive, while that from the sodium is almost wholly emissive. The bottom of the vessel will be somewhat diminished in brightness by the opening opposite giving no radiation to be reflected by it, while the temperature of the sodium being well sustained by the radiation of the sides, the want of radiation from the opening will not make any sensible change in its emission. Whatever explanation be given of the cause, the fact of the gradual expansion of the bright band as the sodium evaporates bears out the supposition that an increased thickness of sodium vapour, with little or no change of density, produces a wider line.

The very minute quantity of sodium required to produce a wide absorption was shewn in the experiments with the amalgams. In one of these .042 gm. of an amalgam containing only $\frac{1}{8}$ per cent. of sodium was introduced into the platinum tube. That quantity of mercury would at 1500° C., which was about the temperature of the furnace, fill about 25 cub. centims., occupying a depth of about 20 centims. of the tube. In this volume there was only about .00005 gm. of sodium, yet the D absorption band was at least twice as wide as the space between the two D lines.

The quantity of sodium requisite to give the channelled spectrum also appears to be very small. Between 4 and 5 mgrms. put into the platinum bottle, whether alone or as an amalgam, usually gave the channelled spectrum; sometimes it was seen with even less than 4 mgrms. Now the wide part of the bottle held some 200 cub. centims., so that the quantity of sodium diffused through this space and up into the tube would give a vapour of very small density indeed. The complete disappearance of the channellings as soon as the vapours were a little compressed, so as to be driven down into the hot part of the bottle, seems to indicate that the channellings were due to comparatively cool vapour in the upper part of the vessel.

The facility with which very high temperatures can be obtained by sudden compression, naturally suggests a repetition of our experiments with the electric arc in lime crucibles, under circumstances in which a pressure of a few atmospheres can be suddenly applied; and this we hope to carry out.

ON THE SPECTRA OF MAGNESIUM AND LITHIUM

[*Proceedings of the Royal Society*, Vol. xxx. (1880), pp. 93 sqq.]

IN a former communication (page 13 above) we described our observations on the absorption spectrum of magnesium, and of magnesium with potassium and sodium, as seen in iron tubes in an atmosphere of hydrogen. These absorptions consisted of—

“(1) Two sharp lines in the green, of which one, which is broader than the other, and appears to broaden as the temperature increases, coincides in position with the least refrangible of the *b* group, while the other is less refrangible and has a wave-length very nearly 5210. These lines are the first and the last to be seen and very constant, and we at first took them for the extreme lines of the *b* group.

“(2) A dark line in the blue, always more or less broad, difficult to measure exactly.

“(3) A third line or band in the green, rather more refrangible than the *b* group....The less refrangible edge of this band is sharply defined, and has a wave-length about 5140, and it fades away towards the blue.

“These absorptions are all seen both when potassium and when sodium are used along with magnesium, and may be fairly ascribed to magnesium, or to magnesium together with hydrogen.

“(4) When sodium and magnesium are used together, a dark line with ill-defined edges is seen in the green, with a wave-length about 5300.

“(5) When potassium and magnesium are used together, a pair of dark lines are seen in the red. The less refrangible of these sometimes broadens into a band with ill-defined edges, and has a mean wave-length of about 6580. The other is always a fine sharp line with a wave-length about 6475.

“(6) On one occasion, with a mixture of potassium and magnesium, another dark line was seen in the blue, with a wave-length nearly 4820.”

We then described the emission spectrum seen when sparks are taken between electrodes of magnesium with a small induction coil without

a Leyden jar as consisting of lines with the wave-lengths 4481, 4590, 4570, 4797, 4930 4945, 4957, 4969, 4980, 4990, 5000, the well-known *b* group, and 5528.

As the absorption lines above described correspond to no known emission lines of magnesium, we could only ascribe their origin to the mixtures employed as distinct from the separate elements, and we were led to investigate the conditions under which corresponding emission lines could be produced.

Shortly afterwards (page 16 above) we described the emission spectrum of sparks from an induction-coil taken between magnesium points in an atmosphere of hydrogen, as follows:—

“A bright line regularly appeared with a wave-length about 5210....This line does not usually extend across the whole interval between the electrodes, and is sometimes seen only at the negative electrode. Its presence seems to depend on the temperature, as it is not seen continuously when a large Leyden jar is employed, until the pressure of the hydrogen, and its resistance, is very much reduced. When well-dried nitrogen or carbonic oxide is substituted for hydrogen, this line disappears entirely; but if any hydrogen or traces of moisture be present, it comes out when the pressure is much reduced. In such cases the hydrogen lines C and F are always visible as well. Sometimes several fine lines appear on the more refrangible side of this line between it and the *b* group, which give it the appearance of being a narrow band shaded on that side.” “In addition to the above-mentioned line, we observed that there is also produced a series of fine lines, commencing close to the most refrangible line of the *b* group, and extending, with gradually diminishing intensity, towards the blue...from forty-five to fifty being visible, and placed at nearly equal distances from each other.”

These observations, though very briefly described, were the result of much labour and many experiments. Mr Lockyer, in a recent communication to the Society, has made this particular emission spectrum the basis of a theory of his own, which we regard as being without any foundation in fact; and as he makes no allusion whatever to our observations, although the abstract of our paper appeared in various scientific journals*, or to the grounds on which we have ascribed the spectrum to a mixture of magnesium with hydrogen, we give now some further details of our former experiments, as well as the observations which we have made since.

* *Nature*, Vol. xviii, pp. 109, 321. *Proc. Camb. Phil. Soc.*, Vol. iii, Part v, p. 208.

1. *Observations on the Spark between Magnesium Points in Nitrogen and Carbonic Oxide at various Pressures.*

The points were pieces of magnesium wire. Round one end of each a platinum wire was tightly coiled and fused into the side of a glass tube. This tube was attached by fusion at one end to another tube filled with phosphoric anhydride, which in turn was connected with a Sprengel pump. The other end of the tube was connected by a thick rubber tube, capable of being closed by a pinchcock, with a gas holder containing nitrogen over strong sulphuric acid. The tube having been exhausted and filled with nitrogen two or three times, it was found that no line at 5210 was visible in the spark. The tube was now gradually exhausted, and the spark watched as the exhaustion proceeded. No line at 5210 was seen, although the exhaustion was carried nearly as far as the pump would carry it; nor was any hydrogen line (C or F) visible, either with or without the use of a jar. The communication with the gas holder was now opened, and the tube refilled with nitrogen at the atmospheric pressure; a communication was then made with another vessel containing hydrogen, which was allowed to diffuse into the tube for a very short time. On now passing the spark, the line at 5210 at once appeared, although the quantity of hydrogen diffused into the nitrogen must have been very small. The experiments with nitrogen at reduced pressure were repeated several times, with the same result. It was found necessary to have the phosphoric anhydride, as without it traces of moisture were left or found their way through the pump into the tube, and then, when the exhaustion was carried far enough, both the line at 5210 and the hydrogen lines, C and F, made their appearance. We have never, however, been able to detect the line at 5210, in nitrogen, without being able to detect C or F either at the same time or by merely varying the discharge by means of a Leyden jar.

Experiments made in the same way with carbonic oxide instead of nitrogen led to precisely similar results.

2. *Observations on the Spark between Magnesium Points in Hydrogen at reduced Pressures.*

A tube, similar to those employed with nitrogen and carbonic oxide, was attached at one end to a Sprengel pump and mercury gauge, and at the other to an apparatus for generating hydrogen. Dry hydrogen was passed through for some time, and the connexion with the hydrogen apparatus closed. On sparking with the hydrogen at the atmospheric pressure, the line at 5210 and its attendant series were visible, and were still visible when a small Leyden jar was used with the induction-coil, but disappeared almost entirely when a large Leyden jar was used. When the pressure of

the hydrogen was reduced to half an atmosphere, the line at 5210 was seen faintly when a large Leyden jar was used, but not the series of fine lines. When the pressure was reduced to 180 millims., the series of fine lines began to shew when the large jar was used. By still further reducing the pressure the whole series was permanently visible when the large jar was used; but when the exhaustion was carried still further they grew fainter, and almost disappeared. On gradually readmitting hydrogen, the same phenomena recurred in the reverse order.

3. *Observations on the Arc with Magnesium and Hydrogen.*

The line at 5210 is not seen in the arc in a lime or carbon crucible when magnesium is dropped in without the introduction of hydrogen. If, however, a gentle stream of hydrogen, or of coal gas, be led in through a perforation in one of the electrodes, the line at 5210 immediately makes its appearance, and, by varying the current, it may be made to appear either bright or reversed. However small the current of hydrogen be made, the line can be detected as long as the current and the supply of magnesium continues, and disappears very quickly when the current ceases.

4. *Observations on the Flame of Burning Magnesium.*

The line at 5210 may often be seen in the flame of magnesium burning in air, but both it and the series of fine lines which accompany it come out with greatly increased brilliance if the burning magnesium be held in a jet of hydrogen, of coal gas, or of steam.

The experiments above described, with nitrogen and carbonic oxide at reduced pressures, are almost, if not quite, conclusive against the supposition that the line at 5210 is due merely to the lower temperature of the spark in hydrogen. From De La Rue and Müller's observations it would appear that nitrogen at a pressure of 400 millims. should produce much the same effect on the spark as hydrogen at 760 millims. Now the pressures of the nitrogen and carbonic oxide were reduced far below this without any trace of the line in question being visible. Moreover, the magnesium line at 4481, which is not seen in the arc, and may be reasonably ascribed to the higher temperature of the spark, may be seen in the spark at the same time as the line at 5210 when hydrogen is present. Nevertheless temperature does seem to affect the result in some degree, for when a large Leyden jar is used, and the gas is at the atmospheric pressure, the line almost disappears from the spark, to reappear when the pressure is reduced; but by no variation of temperature have we been able to see the line when hydrogen was carefully excluded.

A line of the same wave-length has been seen by Young in the chromosphere once. Its absence from the Fraunhofer lines leads to the

inference that the temperature of the sun is too high (unless at special times and places) for its production. If it be not due to a compound of magnesium with hydrogen, at any rate it occurs with special facility in the presence of hydrogen, and ought to occur in the sun if the temperature were not too high.

We have been careful to ascribe this line and its attendant series to a mixture of magnesium and hydrogen rather than to a chemical compound, because this expresses the facts, and we have not yet obtained any independent evidence of the existence of any chemical compound of those elements. We have independent evidence that mixtures which are not probably chemical compounds favour the production of certain vibrations which are not so strong or are not seen at all when the elements of those mixtures are taken separately. The remarkable absorptions produced by mixtures of magnesium with potassium and sodium above-mentioned belong to this class. We have not been able to obtain the emission spectra corresponding to these absorptions, but in the course of our observations on the arc we have frequently noticed that certain lines of metals present in the crucible are only seen or come out with especial brilliance when some other metal is introduced. This is the case with some groups of calcium lines which are not seen, or barely visible, in the arc in a lime crucible, and come out with great brilliance on the introduction of a fragment of iron, but are not developed by other metals such as tin.

The spectrum of magnesium, as seen in the arc, contains several lines besides those heretofore described. These lines come out brightly, generally considerably expanded, when a fragment of magnesium is dropped into the crucible through which the arc is passing, but rapidly contract and gradually become very faint or disappear entirely.

(1) A line in the greenish-yellow, wave-length 5710·7. This line is seen not only in the arc but also when sparks are taken from a solution of magnesium chloride. It is a faint line in the latter case, but is seen in carefully purified samples of the chloride, so that we have no doubt that it belongs to magnesium.

(2) A line, wave-length 4351·2, very close to a chromium line. It is easily distinguished from the latter by its expansion when fresh magnesium is introduced, while the chromium lines shew no expansion; it is moreover slightly more refrangible than the chromium line, and as it dies out it is sharply defined on the less refrangible side, diffuse on the other side. This line frequently appears to be accompanied by another weaker line at wave-length 4355, but we have not been able to assure ourselves that the latter is due to magnesium alone. It is certainly developed when magnesium is introduced, and we do not know of any other element to which it can be ascribed; but it behaves very much as some lines of other elements, *e.g.*, the

violet lines of lithium mentioned below, coming out brightly when magnesium is freshly put in, and then nearly dying away.

(3) A violet line, wave-length 4166, identical in position with the sharp edge of one of the so-called carbon bands in that region.

(4) Another violet line, wave-length 4057·3, easily recognised by its position between two strong iron lines.

These last three lines are conspicuous in Capron's photograph of magnesium in arc. The last (4) may be seen in the spark between magnesium points, and was formerly mistaken by us for the potassium line which is near it. The lines (3) and (4) are so nearly identical in position with two well-known lines of lead, that a suspicion naturally arises that they may be due to the presence of that metal. We can never be sure that the carbons or even the limestone crucibles we have used may not contain traces of lead; but if that be so, and these lines are the consequence, it is certain that these two lines are strengthened in an extraordinary degree by the presence of magnesium, while the other lines of lead are not seen at all. Photographs of the arc taken when a fragment of magnesium is introduced shew these lines strongly, while no trace is discernible of other lead lines 4062, 4246, or 4386. Until we get some other evidence of the presence of lead, we must ascribe these lines to magnesium.

There are lines in the "normal solar spectrum" corresponding to all these lines except that at 4166. That at 5710·7 is ascribed to iron by Ångström, but neither Thalén, Kirchhoff, Huggins, nor Boisbaudran give any iron line at this place; and we have not succeeded in seeing any such iron line, but there is an air-line very nearly in that position. Rutherford's photograph of the solar spectrum shews a line very nearly at 4166.

This makes the spectrum of magnesium in the arc consist of lines at 5510·7, 5527·5, the *b* group, 4703·5, 4570·5, 4351·2, 4166, 4057·3, and the triplet beyond H.

On the Spectrum of Lithium.

In the spectrum of lithium we have not heretofore been able to obtain the wave-length of the violet line (at about 4130, Boisbaudran) by reason of its very diffuse character, but we have recently found that by a slight modification of our apparatus we could obtain this line more sharply defined and even reversed. This modification consists in making the opening in the lime small, 5 or 6 millims. in diameter, using small carbons as electrodes, and the current from a De Meritens machine. The line can then be seen close to but on the less refrangible side of the barium line in that region. We make its wave-length 4131·7.

Besides this line we find that lithium gives another line in the arc at 4273. This line comes out conspicuously nearly midway between one of the brightest chromium lines and an iron line when a fragment of lithium is dropped into the crucible. The same line may also be detected in the spark taken between points of fused lithium carbonate; and as a sample of the carbonate very carefully purified shews this line, we have no doubt that it really belongs to lithium.

Both these lines are remarkably strengthened when a fragment of magnesium is dropped into the crucible.

On taking a photograph of the arc when a fragment of lithium is introduced, two more lines come out on either side of H and K. These are generally diffuse, and barely discernible by the eye in the arc when glass prisms are used, but easily seen with a calcite prism and quartz lenses. In the powerful arc of a Siemens machine they are enormously expanded and reversed. From measurements of the photographs the wave-lengths appear to be 3913 and 3984. A yet more refrangible diffuse line appears in the photographs at about 3799.

The lithium lines form a progression not unlike that of the sodium lines, the alternate lines at 4603, 4131·5, 3913 are much more diffuse than the lines at 4972, 4273, and 3984, and approach nearer together as they become more refrangible. There is probably another narrow line at about 3838, amongst the magnesium triplet, which we have not yet made out with certainty, and we may expect to find fainter lines still more refrangible, but as our photographs have been taken with a train of glass prisms they do not shew out.

There is a line in the "normal solar spectrum" corresponding to the line at 4273.

While the ratios of the wave-lengths of the red, orange, and green lines of lithium are nearly $\frac{1}{20} : \frac{1}{22} : \frac{1}{27}$, those of the green and blue lines and the two violet lines first above-mentioned are nearly $\frac{1}{25} : \frac{1}{27} : \frac{1}{29} : \frac{1}{30}$.

ON THE SPECTRA OF THE COMPOUNDS OF CARBON WITH
HYDROGEN AND NITROGEN

[*Proceedings of the Royal Society*, Vol. xxx. (1880), pp. 152 sqq.]

IN a memoir "On the Spectra of Metalloids" (*Nova Acta Reg. Soc. Upsal.*, Ser. iii, Vol. ix), Ångström and Thalén have made a careful analysis of the different spectra assigned to carbon. They distinguish four sets of groups of shaded bands produced under different circumstances, which they define, besides the line spectrum which they ascribe to carbon itself. Of these four sets of bands, two sets, situated at the extremities of the spectrum, they shew to be produced in the combustion of cyanogen, a third to be common to all the hydrocarbons, and the fourth to be produced by carbonic oxide. The first two sets, the third, and the fourth sets respectively, they observed to be produced also in the electric discharge between carbon electrodes according as it took place in nitrogen, hydrogen, or oxygen. Their observations on this subject appear to us almost conclusive. Nevertheless, other observers have, since their publication, maintained different opinions.

The spectrum of hydrocarbons burning in air has been repeatedly described: first by Swan in 1856, and afterwards by Attfield, Watts, Morren, Plücker, Boisbaudran and others, and has been given in detail by Piazz Smyth ("End-on Illumination in Private Spectroscopy," *Chem. News*, Vol. 39, pp. 145, 166, 188). The characteristic part of this spectrum consists of four groups of bands of fine lines in the orange, yellow, green, and blue respectively, and we refer hereafter to these as the hydrocarbon bands. These four groups, according to Plücker and Hittorf, also constitute the spectrum of the discharge of an induction-coil in an atmosphere of hydrogen between carbon electrodes. They are also conspicuous in the electric discharge in olefiant gas at the atmospheric and at reduced pressures.

The descriptions of the other less conspicuous parts of the spectrum of the flame of hydrocarbons are not all concordant. Boisbaudran notices, besides the four hydrocarbon bands, only two hazy bands in the indigo. Watts (*Phil. Mag.*, 1869 and 1871) and Piazz Smyth give the same two bands somewhat wider, and resolved into a series of fine lines. These two

observers are in substantial agreement about this part of the spectrum, but Piazzzi Smyth notices in addition a faint haze in the red below C.

Plücker and Hittorf notice the entire absence in the flame of olefiant gas of the two bright groups of lines (blue and violet as described below) characteristic of the flame of cyanogen, and the presence of a series of dark lines on a violet background in a position intermediate between those of the two cyanogen groups. A similar description is given by Morren (*Ann. Ch. et Phys.*, Mars, 1865). Neither of these observers notices the two hazy bands above-mentioned. The descriptions given by these authors of this series of dark lines appear to relate to something not seen by the other observers. They resemble in some respects the description of the corresponding part of the spectrum of the electric discharge in vapour of sulphur, and we think it highly probable that these lines were due to some compound of sulphur derived from the sulphuric acid employed in preparing the gas.

Several observers also have described the spectrum of the flame of burning cyanogen. Faraday, as long ago as 1829, called the attention of Herschel and Fox Talbot to it, and the latter, writing of his observations (*Phil. Mag.*, Ser. iii, Vol. iv, p. 114), points out as a peculiarity that the violet end of the spectrum is divided into three portions with broad dark intervals, and that one of the bright portions is ultra-violet. More recently Dibbits, Morren, Plücker and Hittorf have particularly described this spectrum. Dibbits (*Pogg. Ann.*, 1864) mentions in the cyanogen flame fed with oxygen, a series of orange and red bands shaded on the less refrangible side (*i.e.*, in the opposite way to the hydrocarbon bands), the four hydrocarbon bands more or less developed, a group of seven blue lines, a group of two or three faint blue (indigo) lines, then a group of six violet lines, and, lastly, a group of four ultra-violet lines. When the cyanogen is burnt in air the hydrocarbon bands are less developed, and the three faint indigo lines are scarcely visible, but the rest of the spectrum is the same, only less brilliant.

Plücker and Hittorf (*Phil. Trans.*, 1865) state that in the flame of cyanogen burning in air under favourable circumstances, the orange and yellow groups of lines characteristic of burning hydrocarbons are not seen, the brightest line of the green group appears faintly, the blue group is scarcely indicated; but a group of seven fluted bands in the blue, three in the indigo, and seven more in the violet, are well developed, especially the last. When the flame was fed with oxygen instead of air, they state that an ultra-violet group of three fluted bands appeared. They notice also certain red bands with shading in the reverse direction, which are better seen when the flame is fed with air than with oxygen. Other observers give similar accounts, noticing the brilliance of the two series of bands in the blue and violet above-mentioned, and that they are seen equally in the

electric discharge through cyanogen. All do not notice the ultra-violet group, but this is no doubt owing to the absorption of these rays by the prisms employed, for photographs which we have taken of the spectrum of the cyanogen flame in air shew this group strongly developed.

These three bright groups of bands of fine lines are as characteristic of the flame of cyanogen and of the spark in that gas, as the four hydrocarbon bands are of the flame of hydrocarbons.

The flame of carbonic oxide shews nothing but a continuous spectrum. The series of bands seen in the spark in an oxide of carbon are well known, and there is not, so far as we know, any dispute about them. The brightest of them appears to have been seen by some observers in the flame produced by the combustion of other compounds of carbon.

The contention of Ångström and Thalén is that the channelled spectra of the hydrocarbon and cyanogen flames are the spectra of acetylene and cyanogen, and not of carbon itself, and that in the flame of burning cyanogen we sometimes see the spectrum of the hydrocarbon superposed on that of the cyanogen, the latter being the brighter; and that in vacuum tubes containing hydrocarbons the cyanogen spectrum observed is due to traces of nitrogen.

No chemist who remembers the extreme sensibility of the spectroscopic test, and the difficulty, reaching almost to impossibility, of removing from apparatus and material the last traces of air and moisture, will feel any surprise at the presence of small quantities of either hydrogen or nitrogen in any of the gases experimented on.

Mr Lockyer (*Proc. Roy. Soc.*, Vol. xxvii, p. 308) has recently obtained a photograph of the arc in chlorine, which shews the series of fluted bands in the ultra-violet, on the strength of which he throws over the conclusion of Ångström and Thalén, and draws inferences as to the existence of carbon vapour above the chromosphere in the coronal atmosphere of the sun, which, if true, would be contrary to all we know of the properties of carbon. We cannot help thinking that these bands were due to the presence of a small quantity of nitrogen.

Our faith in the conclusions of Ångström and Thalén on this subject has been much strengthened by our own observations, which we now proceed to describe.

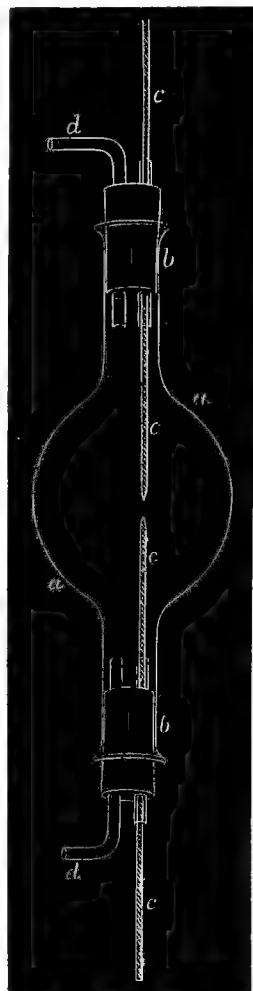
The following experiments were made with a De Meritens magneto-electric machine, arranged for high tension, giving an alternating current capable of producing an arc between carbon poles in air of about 10 millims. in length. The carbon poles were 3 millims. in diameter, and had been previously purified by prolonged heating in a current of chlorine. This treatment, though it removes a large part of the metallic impurities present

in the commercial carbons, will not remove the whole, so that lines of calcium, iron, magnesium, and sodium may still be recognised in the arc. Besides the traces of metallic impurities a notable quantity of hydrogen always remains unremovable by treatment with chlorine; and we are not at present aware of any practicable method by which it can be got rid of.

The arc was taken in different gases inside a small glass globe (*aa* in figure) about 60 millims. in diameter, blown in the middle of a tube. The two ends of the tube (*bb*) were closed with dry corks, through which were passed (1) the carbons (*cc*), inserted through two pieces of narrow glass tubing, and a packing of platinum foil; (2) two other glass tubes (*dd*) through which currents of the gases experimented with were passed.

Spectrum of the Arc in Air.

The arc taken in a globe of air gave a tolerably bright continuous spectrum, superposed on which the green and blue hydrocarbon bands were seen, also the seven bands in the blue (wave-lengths 4600 to 4502, Watts) as in the flame of cyanogen, three faint bands, or lines, in the indigo (wave-lengths about 4364·5, 4371·5, 4381·5), and much more brightly the six bands in the violet (wave-lengths 4220 to 4158, Watts) and five ultra-violet (wave-lengths about 3883·5, 3871, 3862, 3854·5, 3850). Besides these bands, lines of iron, calcium, and sodium were visible. The arc in this case was practically taken in a mixture of nitrogen and carbonic oxide, for in a short time the oxygen of the air is converted into carbonic oxide, as was shewn by the flame which always filled the globe on stopping the arc for a second or two.



Spectrum of the Arc in Carbonic Acid Gas.

On passing through the globe continuously a current of carbonic acid gas, the seven bands in the blue, and those in the violet and ultra-violet, gradually died out until they ceased to be at all visible continuously, and when now and then momentarily seen were only just discernible. On the other hand, the hydrocarbon bands, yellow, green and blue, came out stronger and were even brilliant. Lines of iron and calcium were still visible. On

stopping the current of carbonic acid gas and allowing air to diffuse into the globe, the violet and ultra-violet bands soon began to appear and presently became permanent and bright, the hydrocarbon bands remaining bright.

Spectrum of the Arc in Hydrogen.

The globe had next a continuous current of dry hydrogen passed through it. The arc, contrary to what would be expected from the behaviour of the spark discharge in hydrogen, would not pass through more than a very short space, very much less than in air or carbonic acid gas. There was a tolerably bright continuous spectrum, no trace of the seven bands in the blue, or of those in the violet or ultra-violet, and no metallic lines, but a fairly bright line in the red, which we identified, by comparison with the spark in a vacuum tube, with the C line of hydrogen. The F line, identified in like manner, was also seen as a faint diffuse band. This last line was in general overpowered by the continuous spectrum, but was regularly seen when, from some variation in the discharge, the continuous spectrum became less brilliant. This was the first occasion on which we had seen the hydrogen lines in the arc at all, though Secchi (*Compt. Rend.*, 1873) states that he had seen them by the use of moist carbon poles. We tried to repeat his experiment, without success. The hydrocarbon bands in the green and blue were at intervals well seen. Those in the yellow and orange were, owing doubtless to the smaller dispersion of the light in that region, overpowered by the continuous spectrum. Whereas when air and carbonic acid gas were used, the inside of the globe was quickly covered with dust from the disintegrated poles, scarcely any, if any, such dust was thrown off when the arc was passed in hydrogen.

Spectrum of the Arc in Nitrogen.

Nitrogen was next substituted for the hydrogen. A longer arc would now pass, the seven blue, the violet and ultra-violet bands all came out well, at intervals brilliantly. The green and blue hydrocarbon bands were also well developed.

Spectrum of the Arc in Chlorine.

On filling the globe with chlorine and keeping a current of that gas passing through it, the arc would not pass through a greater distance than about 2 millims. No metallic lines were visible. At first the violet bands, as well as the green and blue hydrocarbon bands, were visible, but gradually when the current of chlorine had been passing for some minutes, there was nothing to be seen but a continuous spectrum with the green and blue hydrocarbon bands. Neither of these bands were strong, and at intervals the blue bands disappeared altogether.

Spectrum of the Arc in Carbonic Oxide.

When the globe, previously full of air, was filled with carbonic oxide and a current of that gas passed through it, the arc would not pass through any greater space than in chlorine. There was much continuous spectrum; the yellow, green, and blue hydrocarbon bands were well seen, some of the seven blue bands were just discernible, the violet had nearly, and the ultra-violet quite, gone from sight. No trace of the carbonic oxide bands, as seen in the spark discharge in that gas, was visible. This is the more remarkable since under similar circumstances two of the characteristic lines of hydrogen were seen.

Spectrum of the Arc in Nitric Oxide.

In this gas a very long arc could be obtained. The violet and ultra-violet bands were well seen, the seven blue bands were seen but weaker. The blue and green hydrocarbon bands were also seen well when the arc was short, not so well when the arc was long. The length of the arc did not seem to affect the brightness of the violet bands. Many metallic lines of iron, calcium, and magnesium were seen.

Spectrum of the Arc in Ammonia.

In ammonia only a short arc could be obtained. All the bands were faint, but the seven blue, the violet and ultra-violet bands were always visible.

These experiments with different gases eliminate to a large extent the influence of electric conductivity on the character of the spectrum; but we intend to examine more thoroughly the effect of this variable by observation of the arc in some of these gases under different conditions of pressure.

Spectra of Flames of Carbon Compounds.

Besides the experiments with the arc above described, we have made some observations of the spectra of flames of sundry compounds of carbon.

In the flame of cyanogen, prepared from well-dried mercury cyanide, passed over phosphoric anhydride inserted in the same tube, and burnt from a platinum jet fused into the end of the tube, we found, as Plücker and Hittorf had found, that the hydrocarbon bands were almost entirely absent, only the brightest green band was seen, and that faintly. The seven blue and the violet bands on the other hand were, as described by other observers, well developed, the three indigo bands less brightly. A series of bands at the red end, also described by Dibbits and by Plücker and Hittorf, was also visible. These bands are sharply defined on the more refrangible side and fade away on the other side, and extend beyond the orange hydrocarbon

bands on the red side. They have not been seen by us in the spectra of the arc, but they may very well have been present in some of those spectra and yet not seen because of the continuous spectrum of the arc, which, not being very much dispersed at the red end, was bright enough to overpower any such bands. This continuous spectrum seems much stronger when well purified carbon electrodes are used than when they contain metallic impurities to the extent commonly present in them. We may remark that in general we see only six bands, or rather six maxima of light, in the violet series, as stated by Dibbits, not seven, as stated by Morren and by Plücker and Hittorf; and in the ultra-violet we always see five maxima of light, instead of four as given by Dibbits, and three given by Plücker and Hittorf. These ultra-violet bands are well developed in the flame of cyanogen burning in air and are readily photographed, and easily seen when quartz lenses and calcite prisms are employed.

The flame of hydrocyanic acid burning in air shewed very much the same as that of cyanogen.

In the flame of a mixture of hydrogen and carbon disulphide, made by passing purified hydrogen through a tube containing carbon disulphide so as to be nearly or quite saturated with the vapour, and burning it in air, no hydrocarbon bands at all could be detected.

Nor could any hydrocarbon bands be detected in the flame of a mixture of carbonic oxide and hydrogen burnt in air.

When a mixture of hydrogen with carbon tetrachloride vapour was burnt, hydrocarbon bands made their appearance, but were rather weak.

The flame of carbonic oxide mixed with vapour of carbon tetrachloride shewed faint traces of hydrocarbon bands occasionally, but not continuously.

On the other hand, chloroform, carefully prepared from chloral and fractionated, when mixed with hydrogen gave, when burnt in air, the hydrocarbon bands very strongly. When it was mixed with carbonic oxide instead of hydrogen it still gave the hydrocarbon bands, but not nearly so strongly as with hydrogen.

On a review of the whole series of observations, certain points stand out plainly. In the first place, the seven blue, the violet, and ultra-violet bands, characteristic of the flame of cyanogen, are conspicuous in the arc taken in an atmosphere of nitrogen, air, nitric oxide, or ammonia, and they disappear, almost if not quite, when the arc is taken in a non-nitrogenous atmosphere of hydrogen, carbonic oxide, carbonic acid, or chlorine. These same bands are seen brightly in the flames of cyanogen and hydrocyanic acid, but are not seen in those of hydrocarbons, carbonic oxide, or carbon disulphide. The conclusion seems irresistible that they belong to cyanogen; and this conclusion does not seem to us at all invalidated by the fact that

they are seen weakly, or by flashes, in the arc or spark taken in gases supposed free from nitrogen, by reason of the extreme difficulty of removing the last traces of air. They are never, in such a case, the principal or prominent part of the spectrum, and in a continuous experiment they are seen to fade out in proportion as the nitrogen is removed. This conclusion is strengthened by the observations of one of us, that cyanogen (or hydrocyanic acid) is generated in the arc in atmospheric air in large quantity. Also in the experiment above described with the arc in nitrogen, we have found that when the current of nitrogen issuing from the globe is passed through a solution of potash the solution soon gives the reactions of a cyanide.

In the next place, the green and blue bands, characteristic of the hydrocarbon flame, are well seen when the arc is taken in hydrogen; but though less strong when the arc is taken in nitrogen or in chlorine, they seem to be always present in the arc, whatever the atmosphere. This is what we should expect, if they be due, as Ångström and Thalén suppose, to acetylene; for we have found that the carbon electrodes always contain, even when they have been long heated in chlorine, a notable quantity of hydrogen.

In the flames of carbon compounds they by no means always appear; indeed, it is only in those of hydrocarbons or their derivatives that they are well seen. Carbonic oxide and carbon disulphide, even when mixed with hydrogen, do not shew them; and if seen in the flames of cyanogen, hydrocyanic acid, and carbon tetrachloride mixed with hydrogen, they are faint, and do not form a principal or prominent part of the spectrum. This is all consistent with the supposition of Ångström and Thalén. The fact that the bands are not produced even in the presence of hydrogen, when it is not present in the flame in the form of a compound with carbon, is very significant; for we know that acetylene is present, and can easily be extracted from the flame of any hydrocarbon, and that it is formed as a proximate product of decomposition of hydrocarbons by the electric discharge, but we have no evidence that it is producible as a product of direct combination of carbon with hydrogen at the comparatively low temperature of a flame such as we have mentioned.

The hydrocarbon bands are best developed in the blowpipe flame, that is under conditions which appear, at first sight, unfavourable to the existence of acetylene in the flame. We have, however, satisfied ourselves, by the use of a Deville's tube, that acetylene may readily be withdrawn from the interior of such a flame, and from that part of it which shews the hydrocarbon bands most brightly.

The question as to whether these bands are due to carbon itself or to a compound of carbon with hydrogen, has been somewhat simplified by the

observations of Watts and others on the spectrum of carbonic oxide. There is, we suppose, no doubt now that that compound has its own spectrum quite distinct from the hydrocarbon flame spectrum. The mere presence of the latter spectrum feebly developed in the electric discharge in compounds of carbon supposed to contain no hydrogen, appears to us to weigh very little against the series of observations which connect this spectrum directly with hydrocarbons.

In the next place, it appears conclusively from the experiments, that the development of the violet bands of cyanogen, or the less refrangible hydrocarbon bands, is not a matter of temperature only. For the appearance of the hydrogen lines C and F in the arc taken in hydrogen, indicates a temperature far higher than that of any flame. Yet the violet bands are not seen in hydrogen at that temperature, while the green bands are well developed. The violet bands are, nevertheless, seen equally well at the different temperatures of the flame, arc, and spark, provided cyanogen be the compound under observation in the flame, and nitrogen and carbon are present together at the higher temperatures of the arc and spark.

The similarity in the character of the magnesium-hydrogen spectrum, which we have described, to the green band of the hydrocarbons is very striking. We have similar bright maxima of light, succeeded by long drawn out series of fine lines, decreasing in intensity towards the more refrangible side. This peculiarity, common to both, impels the belief that it is a consequence of a similarity of constitution in the two cases, and that magnesium forms with hydrogen a compound analogous to acetylene. In this connexion the very simple relation (2:1) between the atomic weights of magnesium and carbon is worthy of note, as well as the power which magnesium has, in common with carbon, of combining directly with nitrogen. We may with some reason expect to find a magnesium-nitrogen spectrum.

Apart from the mere relative electric conductivity of gases, it is clear, from the foregoing experiments, that the length and the character of a discontinuous electric discharge in different gases does not follow the law which we should expect. It will require a prolonged series of experiments to arrive at definite conclusions on this matter, but it appears to us, in the meantime, highly probable that one of the main factors in producing these remarkable variations in the arc will be found to be the relative facility with which the carbon electrode combines with a gaseous medium.

The interest attaching to the question of the constitution of comets, especially since the discovery by Huggins (*Proc. Roy. Soc.*, xvi, p. 386; xxiii, p. 154; *Phil. Trans.*, 1868, p. 555) that the spectra of various comets are all identical with the hydrocarbon spectrum, naturally leads to some speculation in connexion with the conclusions to which our experiments point. Provided we admit that the materials of the comet contain ready

formed hydrocarbons and that oxidation may take place, then the acetylene spectrum might be produced at comparatively low temperatures without any trace of the cyanogen spectrum, or of metallic lines. Such reactions might be brought about by the tidal disturbances involving collisions and projections of the constituents of the swarms of small masses circulating in orbits round the sun, which we have every reason to believe constitute the cometic structure. If, on the other hand, we assume only the presence of uncombined carbon and hydrogen, we know that the acetylene spectrum can only be produced at a very high temperature; and if nitrogen were also present, that we should have the cyanogen spectrum as well. Either then the first supposition is the true one, not disproving the presence of nitrogen; or else the atmosphere which the comet meets is hydrogen and contains no free nitrogen.

NOTE ON THE HISTORY OF THE CARBON SPECTRUM

[*Proceedings of the Royal Society*, Vol. xxx. (1880), pp. 490 sqq.]

IN a "Note on the Spectrum of Carbon," read before the Society on April 29, 1880 (*Proc. R. S.*, xxx, p. 335), Mr Lockyer has in the first place alleged that we have advanced within a very short period inconsistent opinions as to spectra of compounds of carbon; he has next implied that we have given an unfair representation of the history of the carbon spectrum, and, lastly, has directly challenged the correctness of some of the conclusions we have drawn from our experiments. We propose in this paper to reply to him on the historical questions, and in another paper to deal with the experimental evidence which he has produced in contravention of our conclusions.

That the inconsistency alleged has not really existed in our opinions, will be seen by any one who reads the first passage referred to as it appeared in the published *Proceedings of the Society* (Vol. xxx, p. 87), which stands as follows:—

"The well-nigh impossible problem of eliminating hydrogen from masses of carbon, such as can be employed in experiments of this kind, proves conclusively that the inference drawn by Mr Lockyer as to the elementary character of the so-called carbon spectrum from an examination of the arc in dry chlorine, cannot be regarded as satisfactory, *seeing that undoubtedly hydrogen was present in the carbon* and in all probability nitrogen in the chlorine.*"

Mr Lockyer has quoted the *confidential, uncorrected, proof* instead of the published paper which had been issued before Mr Lockyer's paper was read. In the published paper a clause, accidentally omitted before, and no way altering the general drift of the passage, had been inserted to make the sense clearer. The paper from which he quotes deals with the chemical interactions taking place in the arc between the matter of the poles and the constituents of the surrounding atmosphere. It is there demonstrated that specially purified carbon poles continue to produce in dry air cyanogen

* Mr Lockyer having italicised the former half of the last clause, we italicise what he chose to omit.

compounds, and that hydrogen always forms an essential ingredient of such poles. No reference was made in this paper to the specific origin of any flutings in the spectrum of the arc, the sole question under consideration being the possible existence of carbon compounds in the electric arc taken in dry chlorine, on the non-existence of which Mr Lockyer bases his proof of the elementary character of the carbon spectrum. That part of the paper from which the quotation is taken related particularly to the combination of nitrogen with the carbon of the poles, and the final clause added in the published paper accords with it.

There is no inconsistency between the opinion there expressed and that subsequently given in the paper "On the Spectra of the Compounds of Carbon with Hydrogen and Nitrogen"; and that such a charge could have been made is due only to Mr Lockyer's having quoted the *uncorrected proof*.

To come to the omissions we have made in reference to the work of others. The complaints appear in such remarks as the following, which we extract from Mr Lockyer's paper:—

"As Messrs Liveing and Dewar do not controvert the very definite conclusions arrived at by Attfield, Morren, Watts, and others, I can only presume that they have taken for granted that the experimental work performed by these men was tainted by the presence of impurities, and that it was impossible to avoid them."

"The only reference to this admirable work, in which vacuum tubes and the electric discharge were largely employed, which I can find in Messrs Dewar and Liveing's paper is the following:—'The spectrum of hydrocarbon *burning in air* has been...described...by Attfield.'"

It was not our intention to give a complete historical account of what had been done previous to the date of the paper by Ångström and Thalén (*Nova Acta Reg. Soc. Upsal.*, 1875), as in that paper they had discussed the observations of experimenters who had been engaged on this subject before that time. Nor had we any desire to avoid or controvert, or take anything for granted, in the work of early investigators. We merely passed over for the sake of brevity such work as had not stood the test of subsequent investigation. We could hardly accept Dr Attfield's work, however good for its time, as authoritative, seeing that his experiments were made, as he allows (*Phil. Mag.*, 1875), with very imperfect appliances, and evidently without his being so well aware as we now are of the nicety required in regard to the purity of his materials. In fact, he found no distinction between the spectrum of carbonic oxide and that of hydrocarbons, and found the lines of nitrogen in the spectrum of the flame of cyanogen.

We can hardly be charged with ignoring Morren's work, for we have referred to it again and again. The particular passage quoted by Mr Lockyer

embodies observations and conclusions which are at variance with those of Plücker and Hittorf, as well as of Watts; and are substantively discussed by us in our paper.

Dr Watts' position with reference to this subject deserves very special consideration, as he has perhaps directed his attention to it more continuously and laboriously than any other investigator. And as his publications have extended over a long period of years, it is clear that a grave injustice is done him if his early work be selected for quotation instead of the maturer product of his latest study. This kind of selective quotation does not represent the true scientific spirit.

The quotation from Dr Watts' paper (*Phil. Mag.*, 1869) which Mr Lockyer prefaces by this remark—"His work was thus summarised by himself,"—has in reality no reference to a complete summation of his experiments, but has solely to do with "the typical form of the first carbon spectrum that obtained when olefiant gas and oxygen are burnt together in an oxy-hydrogen blowpipe jet." That this is the correct view of Dr Watts' position, the following extracts will shew:—"The spectrum obtained from cyanogen varies with the mode of production. The flame of cyanogen in oxygen exhibits γ , δ , and ϵ . The red group is replaced by a series of bands which shew an opposite character to the rest of the spectrum, inasmuch as each band is brightest at the most refracted edge. If cyanogen be burnt in air instead of in oxygen these bands are more numerous, extending nearly to δ , and replacing γ , which is then not to be seen. Instead of the group f we have two very brilliant groups of lines— ζ , which includes seven lines, and θ , which is composed of six lines."

The two very brilliant groups of lines which are referred to as ζ and θ by Watts, and which distinguish the flame of cyanogen, are two of the sets of channelled groupings which we, in our paper on "The Spectra of the Compounds of Carbon with Hydrogen and Nitrogen," referred to a compound of carbon with nitrogen. Further on, in the same paper of Dr Watts, the following occurs:—"In comparing the spectra of fig. 1, we notice that the changes take place at the ends of the spectra, the central groups, γ , δ , ϵ , remain substantially the same. If we pass from the spectrum of the olefiant gas-flame to that of the cyanogen-flame, we find the change at the blue end of the spectrum consisting in the disappearance of the group f and its replacement by the groups ζ and θ . The group f is not absolutely proved to belong to carbon (that is, it may be caused by carbonic oxide or carbonic anhydride); but the groups ζ and θ , since they are common to carbonic oxide, cyanogen, and naphthalin, must be due to carbon, and their presence may, with much probability, be attributed to the higher temperature of the cyanogen-flame*."

* When Mr Lockyer makes the following statement:—"I have also repeated Morren's experiment and confirmed it, and I have also found that the undoubted spectrum of cyanogen is visible

On the ground of observing these two characteristic groups of lines ζ and θ (our seven blue and six violet nitrocarbon bands) in the spark spectra of carbonic oxide, cyanogen, and naphthalene, Dr Watts was entitled at the time to infer that they must be due to the common element carbon. Dr Watts has, however, made many experiments on the carbon spectrum since the date of that paper, and to neglect to take into consideration papers published by him since 1869 is to misrepresent his position. In the *Phil. Mag.* for 1874, he wrote in a "Note on the Carbon Spectrum" as follows:—"In the *Phil. Mag.* for October, 1869, I described four different spectra as spectra of *carbon*. One of them was the ordinary spectrum from hydrocarbon flames first described by Swan; the second was the spectrum obtained from vacuum tubes inclosing carbonic oxide, carbonic anhydride, or olefiant gas; the third was the spectrum of the Bessemer flame, and the fourth the spectrum of the high tension spark in carbonic anhydride or carbonic oxide.

"I have since shewn (*Phil. Mag.*, Feb. 1873) that the Bessemer flame spectrum, instead of being a spectrum of carbon, is the spectrum of manganese oxide; and I have had now to add the result of recent observations which shew that the second spectrum also is due not to carbon itself, but to some *oxide* of carbon. This spectrum was held to be a spectrum of carbon because it was common to compounds of carbon with hydrogen and with oxygen.

"I have now found that it is not given by spectral tubes inclosing olefiant gas if special care be taken to exclude all trace of oxygen.... We have therefore only one spectrum which can be proved to be due to *carbon*—that, namely, which is common to the flame of olefiant gas or cyanogen, the electric discharge in cyanogen or carbonic oxide at the ordinary pressure, and to the electric discharge in vacuum tubes inclosing cyanogen, olefiant gas, or hydrocarbons such as benzol."

We infer from this, that the groups ζ and θ (our seven blue and six violet nitrocarbon bands), which are certainly not common to all the spectra here enumerated, are not included in the one spectrum which Dr Watts at that time assigned to carbon. However that may be, it is unnecessary to say more about it here, for we have quoted enough to shew that Dr Watts' conclusions, in 1869, were not so certain that they could now be quoted as

neither in the electric arc nor in the surrounding flame,"—he is referring to a different part of the spectrum altogether from the one we have been discussing, and the application of the term "undoubted" to the specific part of the spectrum to which he here refers is simply an expression of his own view. Ångström and Thalén in their *Recherches sur les Métalloïdes*, 1875, have the following passage:—"Les groupes nuancés de cyanogène, situés dans les parties bleues et violettes du spectre, se montrent aussi, soit quand l'étincelle traverse la partie luisante d'une flamme à gaz, soit dans l'arc voltaïque entre des électrodes du charbon d'une pile puissante. Cependant, ce dernier spectre du cyanogène, qui est remarquable par l'éclat vif des raies, n'est pas pur, mais mêlé des raies des carbures d'hydrogène, dont le splendeur est encore plus magnifique."

authoritative against the inferences drawn from later observations, and that we did our subject no injustice in making no more particular allusions to them than we did.

But, further, after describing an experiment with carbon tetrachloride, Mr Lockyer says:—"This result, which entirely endorses the work of Attfield and Watts, has been controlled by many other experiments." If we may assume that the work of Attfield and Watts alluded to is that described in the previous quotations, it is not a little remarkable that Mr Lockyer's experiments should so "entirely endorse" what Watts himself has shewn to have been in part erroneous.

Lastly, we cannot allow Mr Lockyer's assertion that Ångström and Thalén's conclusions "rest more upon a theory which has been shewn to be false since the labours commenced, and analogy, than upon experiment," to remain uncorrected. Their conclusions are eminently inductions from experiments carried on, as they say, during several years, of which the most important are particularly described. Many of the experiments which led up to their conclusions had been previously published by Thalén in 1866 (*Årsskrift, Upsala*), in a paper in which he correctly described and distinguished the spectra of hydrocarbons, of oxide of carbon, and of carbon respectively, and besides described the spectrum of the spark between carbon poles in nitrogen. This paper is an admirable sample of good experimental work, and its perusal, together with the later paper of 1875, leaves no doubt that, whatever theories they may have held, Ångström and Thalén relied mainly on experiment and observation to prove the soundness of their conclusions.

In conclusion, Mr Lockyer introduces a reference to a former work of ours on the magnesium-hydrogen spectrum, and to a theoretical deduction regarding the interactions which might produce the cometic spectrum, making the following remark:—

"From what I have shewn it will be clear that the consequences drawn in the following paragraphs by Messrs Liveing and Dewar from the assumed hydrogen-carbon bands are entirely invalid."

As this opens out a question entirely beside that in hand, depending on the validity of the premises from which Mr Lockyer draws his conclusion, we prefer to deal with it when we discuss, in our next paper, the spectra of carbon compounds and the experimental evidence Mr Lockyer has adduced in support of such assertions.

ON THE SPECTRA OF THE COMPOUNDS OF CARBON
WITH HYDROGEN AND NITROGEN. No. II.

[*Proceedings of the Royal Society*, Vol. xxx. (1880), pp. 494 sqq.]

IN our last communication on this subject (*ante*, p. 85), we thus summarised the results of our observations as to the "nitrocarbon spectrum*."

"On a review of the whole series of observations, certain points stand out plainly. In the first place, the seven blue, the violet, and ultra-violet bands, characteristic of the flame of cyanogen, are conspicuous in the arc taken in an atmosphere of nitrogen, air, nitric oxide, or ammonia, and they disappear, almost if not quite, when the arc is taken in a non-nitrogenous atmosphere of hydrogen, carbonic oxide, carbonic acid, or chlorine†. These same bands are seen brightly in the flames of cyanogen and hydrocyanic acid, but are not seen in those of hydrocarbons, carbonic oxide, or carbon disulphide. The conclusion seems irresistible that they belong to cyanogen; and this conclusion does not seem to us at all invalidated by the fact that they are seen weakly, or by flashes, in the arc or spark taken in gases supposed free from nitrogen, by reason of the extreme difficulty of removing the last traces of air. They are never, in such a case, the principal or prominent part of the spectrum, and in a continuous experiment they are seen to fade out in proportion as the nitrogen is removed. This conclusion is strengthened by the observations of one of us, that cyanogen (or hydrocyanic acid) is generated in the arc in atmospheric air in large quantity."

The observations and experiments which we have since made all tend to confirm the correctness of the foregoing induction, while they help to remove the apparent inconsistency of some recorded observations with our conclusions. More particularly they explain the appearance of the bands which we, in common with Ångström and Thalén, have ascribed to a compound of carbon with nitrogen, in some cases in which nitrogen had been supposed to

* In using this term we merely mean that we are dealing with a spectrum invariably associated with the presence of nitrogen and carbon in such conditions that chemical union takes place, without any reference to the particular compound produced.

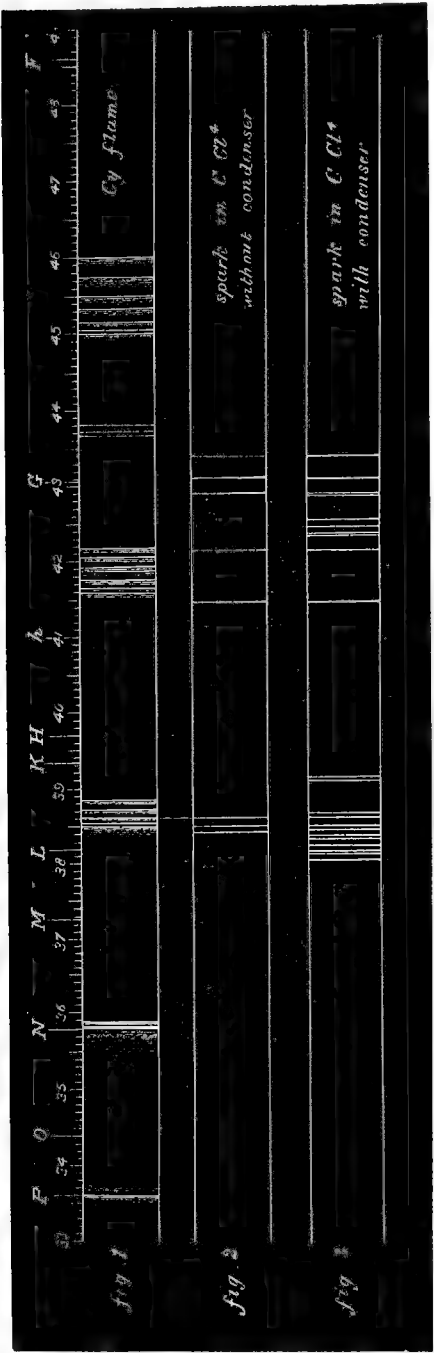
† We have repeated and confirmed the experiments with the De Meritens arc in different gases. The arc examined in different *liquids* also supports the original conclusions.

be absent, by shewing the sensibility of the spectroscopic test for nitrocarbon compounds under varied circumstances, and the consequent necessity for something more than ordinary care in the preparation of materials and conduct of experiments, if inferences dependent on the presumed absence of nitrogen (or hydrogen, as the case may be) are to be drawn from them.

The Flame of Cyanogen.

The accompanying diagram (fig. 1) shews approximately the relative position of the bands in that part of the spectrum of the flame of cyanogen fed with a jet of oxygen which is more refrangible than the Fraunhofer line F. Only those bands which are less refrangible than the solar line L have been before described, but photographs shew another set of two shaded bands slightly less refrangible than the solar line N accompanied by a very broad diffuse band of less intensity on the more refrangible side of N; also a strong shaded band, which appears to be absolutely coincident with the remarkable shaded band in the solar spectrum, which has been designated by the letter P; and near this, on the more refrangible side, a much fainter diffuse band, which also seems to coincide with a part of the solar spectrum sensibly less luminous than the parts on either side of it. This spectrum is remarkably persistent at all temperatures of the flame. Watts found that it did not disappear when the flame was cooled down as much as possible by diluting the cyanogen with carbonic acid; and we have found that it retains its characters when the cyanogen is burnt in nitric oxide. The flame in the last case must be one of the hottest known, from the large amount of heat evolved in the decomposition of cyanogen and nitric oxide, namely, 74,500 and 43,300 units per molecule respectively. There is in the case of cyanogen, as in the case of so many other substances, a difference in the relative intensities of the different parts of the spectrum of the flame at different temperatures, but no other change of character; and we are unable to confirm the observation of Watts, that cyanogen burning in oxygen gives only the bands which we assign to hydrocarbons. It is true, that in the upper part of the flame where much or all of the cyanogen is oxidised or decomposed the spectrum is continuous, but at the base of the flame where it is issuing from the nozzle we have always seen the nitrocarbon bands, both when the cyanogen is burning in oxygen and when it is burning in nitric oxide.

On the theory that these groups are the product of an exceptional temperature in the case of the cyanogen flame, it is inconceivable that they could disappear by combustion in oxygen, instead of in ordinary air. Our observations accord with the statement of Morren, Plücker, Hittorf, and Thalén, that a cyanogen flame, fed with oxygen, when it is intensely luminous, still yields these peculiar groups. We have found these peculiar



groupings in the flame when it had a current of oxygen in the middle, and was likewise surrounded outside with oxygen. There is nothing remarkable in observing only a continuous spectrum from any hydrocarbon or nitrocarbon by using excess of oxygen, as we know from Frankland's experiments that carbonic acid and water vapour at the high temperature of flame under compression gives a continuous spectrum. In fact, this is what we should anticipate, provided intermediate, and not the final, compounds are the active sources of the banded spectrum.

Each of the five sets of bands shewn in the diagram is attended on its more refrangible side by a series of rhythmical lines extending to a considerable distance, not shewn in the diagram, but easily seen in the photographs.

Coal gas burning in oxygen gives no bands above that near G within the range of the diagram, fig. 1, nor are the visible cyanogen bands seen in the flames of many organic compounds containing combined nitrogen; but beyond this our photographs shew a spectrum of a character quite different from that at the less refrangible end. The most remarkable part of this spectrum is a long series of closely set strong lines, filling the region between the solar lines R and S, and ending abruptly with two strong lines a little beyond S. These are lines of various intensities, not regularly arranged so as to give shaded bands like those in the less refrangible part of the spectrum. Beyond these lines there is another large group of lines, not so strong or so closely set, but sharp and well defined. It will be a work of time to examine in detail this very striking and peculiar spectrum; at present we can only indicate its general character. We are not yet sure whether it is produced by pure hydrocarbons, or may not be due to impurities such as sulphur in the coal gas*

Spark Discharge in Carbon Tetrachloride.

We have conducted the experiments with carbon tetrachloride with great care and numerous repetitions on account of the prominence given to an experiment with this compound by Mr Lockyer, in a recent "Note on the Spectrum of Carbon" communicated to the Society, and because our results in every case differ from those which he obtained.

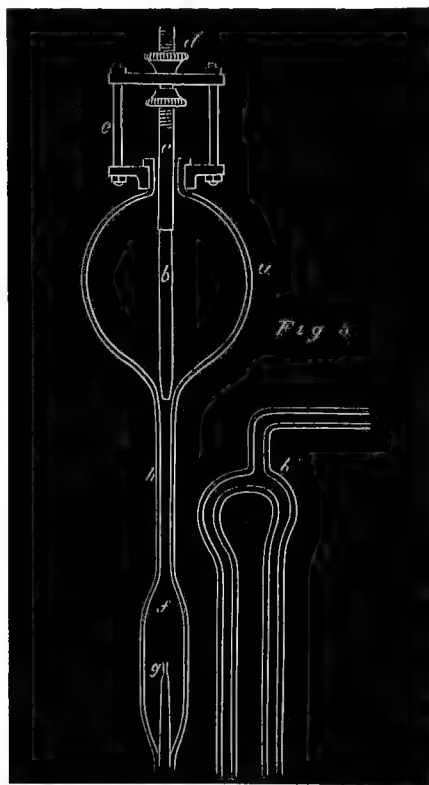
The form of sparking tube employed was similar to that used by Salet, and is shewn in the annexed diagram, fig. 4. This was attached by thick rubber tubing to a straight glass tube of which one half, about 6 inches long, was filled with phosphoric anhydride, and the other half with small

* Since this passage was written we have found reason to believe that this remarkable spectrum is due not to any carbon compound, but to water. As this takes it beyond the scope of the present paper, we purpose dealing with it hereafter in a separate communication. June 8, 1880.

fragments of soda-lime to prevent any chlorine from the decomposition of the tetrachloride by the spark from reaching the pump. The pump was connected by rubber tubing to that end of the tube which contained soda-lime. The tetrachloride used had been prepared in our own laboratory from



carbon disulphide, and fractionated until it had a constant boiling point of 77°C . Sufficient of it was introduced into the sparking tube to fill nearly one quarter of the bulb at the end, and the whole interior of the tube thoroughly wetted with it in order to facilitate the removal of the last traces of air.



The Sprengel pump employed differs slightly from those in common use. The reservoir is a globe funnel (*a*, fig. 5), and the valve formed by a glass

rod (*b*) with a conical termination ground into the neck of the funnel. This rod at its upper end passes into an iron ferule (*c*), which, by means of a screw and a small frame fixed at the top of the globe, can be raised or lowered at pleasure. A little below the globe the tube expands, and the lower part of the tube enters this expansion, and terminates upwards in a narrow tube of platinum, round which the glass is fused. By this means the mercury is continually drawn from the centre of a mass of mercury, and there is less chance of air descending with it. Moreover, as the exhaustion proceeds the part of the tube *h*, above the level of the fall *k*, becomes vacuous, and is an effectual trap for any air which may be sucked down with the mercury from the globe. The necessity for such a trap is apparent, for when the pump has been in continued use for two or three days there is always a small bubble of air collected in *h*.

When the tube containing the tetrachloride had been so far exhausted that little but condensible vapours were pumped out, the bulb was heated so as to fill the apparatus with vapour of tetrachloride, the pump still going, and this was repeated as long as any incondensable gas was extracted. Sparks were then passed through the tube for a short time, the pump still being kept going. After a short time it was unnecessary to keep the pump going, as all the chlorine produced by decomposition of the tetrachloride was absorbed by the soda-lime. On now examining the spectrum, no trace of any of the bands we ascribe to nitrocarbons could be detected, either by the eye or by photography, however the spark might be varied. The violet lines of chlorine described by Salet were more or less visible, coming out brightly when a condenser was used. Several tubes were treated in this way, and many photographs taken, but always with the same result; no trace appeared of either the seven blue, the six violet, the five ultra-violet, or of the still more refrangible bands of the cyanogen flame. It is true that all the photographs shewed three lines in the ultra-violet, but these do not at all closely resemble the nitrocarbon bands: they are not shaded like the nitrocarbon bands. The least refrangible of the three is coincident with the middle maximum in the ultra-violet set of five bands, but the other two do not coincide with other of these maxima. When a condenser is used these three lines come out with much greater intensity, and two other triplets appear on the more refrangible side, as well as other lines. In order to compare the positions of these lines with the cyanogen bands, we have taken several photographs of the spark in tetrachloride simultaneously with a cyanogen flame, the latter being thrown in by reflection in the usual way. Wratten and Wainwright's instantaneous dry plates were used, and gave a strong picture of the cyanogen flame after three seconds' exposure, but in order to ensure getting a picture of all the lines which the spark could produce, we gave an exposure of three minutes to the spark. Not one of many photographs so taken shewed any traces of the cyanogen bands. The

general character of the violet part of the spectrum of the spark in carbon tetrachloride taken without a condenser, but not the exact position to scale of wave-lengths of all the lines, is shewn in Diagram 1, fig. 2. Fig. 3 of the same diagram shews the brightest of the additional lines which come out with the use of a condenser. Photographs of sparks taken in hydrochloric acid shewed a precisely similar group of ultra-violet lines, so that we have no doubt that the three lines which our photographs shew amongst the five ultra-violet nitrocarbon bands are due to chlorine.

A bulb tube was next partly filled with tetrachloride, the end drawn out to a long narrow neck, and the tetrachloride boiled out in an oil-bath (150°C.) so as to expel all air, and the tube sealed off. This tube likewise shewed no nitrocarbon bands.

A bulb was then blown in the middle of a piece of narrow glass tubing, and platinum wires sealed into it; some carbon tetrachloride was introduced into the bulb, and a current of hydrogen passed through the tube at atmospheric pressure; when the air was judged to be expelled sparks were passed by means of the wires in the bulb, but no nitrocarbon bands could be detected. In this case the rapid deposit of carbon soon brought the observations to a close, but the result was the same as before.

Solid trichloride was next tried. It was introduced into a tube similar to that described above in the first experiment with tetrachloride, and treated as the tetrachloride had been, the trichloride being mostly sublimed over into the small bulb shewn in fig. 4, *b*. The trichloride was found to behave, as far as the spectrum is concerned, very much as the tetrachloride had done. It gave no nitrocarbon bands at all.

Having satisfied ourselves by repeated trials that pure carbon chloride if free from nitrogen does not give any of the bands we ascribe to nitrocarbon compounds, our next step was to determine whether the addition of nitrogen would bring them out, and if so what quantity of nitrogen would make them visible. For this purpose we first loosened the binding of the rubber tube connecting to the pump a sparking tube containing tetrachloride, and found to give no nitrocarbon bands, and, after letting in very little air, immediately closed it again. On now passing the spark the six violet bands at once appeared, and soon became quite bright, the seven blue bands were not seen immediately the air was admitted, but they too were in a short time well seen.

After trying some other experiments of a similar kind which indicated that a very small quantity of nitrogen was sufficient to develop the nitrocarbon bands in one of these tubes, we introduced a minute fragment of bichromate of ammonia, carefully weighed, and wrapped in platinum foil, into the neck of one of the sparking tubes containing carbon tetrachloride, connected the tube to the Sprengel pump, and removed the air as before.

On examination of the spark with the spectroscope no trace of any nitrocarbon band could be detected. A pinch-cock was now put on the rubber tube, and the bichromate was heated by a spirit lamp to decomposition (whereby it is resolved into nitrogen, water, and oxide of chromium). On now passing the spark the six violet bands were well seen. There was no change in the condition of the coil or rheotome, so that the spark was of the same character as it had been before when no nitrocarbon bands were visible, and the change in the spectrum cannot be attributed to any change in the spark. The weight of the bichromate was between .0005 and .0006 grm.; and the nitrogen this would evolve would fill just about $\frac{1}{20}$ of a cubic centimeter at atmospheric pressure. The tube held 30 cub. centims., so that vapour of carbon tetrachloride when mixed with $\frac{1}{200}$ part of its volume of nitrogen, gives under the action of the electric spark the nitrocarbon bands distinctly. Other similar experiments confirmed this result. It is worthy of remark that the nitrocarbon bands were not seen instantaneously on the admission of nitrogen into the tube, but were gradually developed, as if it was necessary that a certain quantity of nitrocarbon compound should be formed under the influence of the electric discharge and accumulated before its spectrum became visible.

Spark Discharge in other Compounds of Carbon.

Some carbon bisulphide was introduced into another tube, which was drawn out to a long narrow neck, and the carbon bisulphide boiled out in an oil-bath at 200° C., and the tube sealed off. In the spectrum of the spark taken in this tube no nitrocarbon bands, either blue or violet, could be detected however the discharge was varied.

A similar tube, containing benzene and similarly treated, shewed no trace of the nitrocarbon bands.

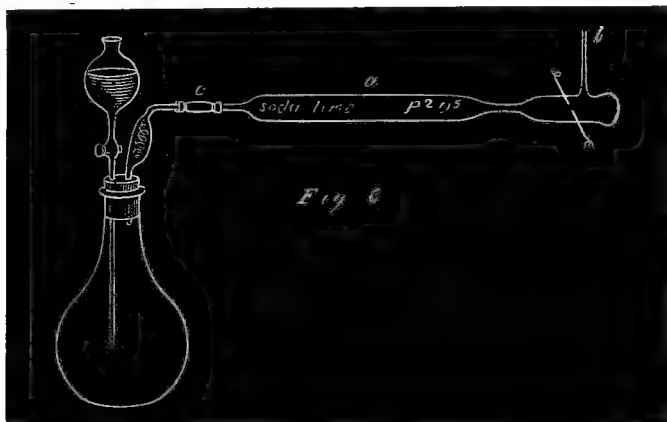
Another tube, containing naphthalene, previously well washed with dilute sulphuric acid, dried and resublimed, was attached to the Sprengel pump, and treated as the tubes with tetrachloride had been. The spark in this tube likewise shewed no nitrocarbon bands. After a time the tube cracked, and then the nitrocarbon bands made their appearance, and on setting the pump going a good deal of gas was pumped out. When the air had again been pretty completely exhausted, the nitrocarbon bands no longer shewed, but gradually reappeared again as air leaked through the crack. Another tube, containing a mixture of naphthalene and benzene, shewed no trace of the nitrocarbon bands.

The observation of the nitrocarbon bands in the spectrum of the spark in naphthalene was one of the reasons which led Watts at one time to ascribe these bands to carbon only. Naphthalene is not well adapted to be the subject of a test experiment in this case, for, from its mode of preparation, it is

liable to be contaminated with nitrogenous bases; and the tension of its vapour at ordinary temperatures is so small that, unless the supply is kept up by heating the tube, the spark soon so far decomposes it that the spectrum is reduced to that of hydrogen only. It appears, however, from our experiments, that if the naphthalene is sufficiently purified and freed from air it does not furnish the nitrocarbon spectrum.

As Watts laid much stress on the occurrence of the nitrocarbon bands in the spectrum of the spark taken in carbonic oxide at atmospheric pressure, though they do not appear in carbonic oxide at reduced pressures, as a proof that these bands were due to carbon only, we have made a series of careful experiments with carbonic oxide at atmospheric pressures.

In our first experiments with this substance the gas was made by the action of sulphuric acid on dried formate of sodium. The dried formate was placed in a flask (fig. 6) fitted with a rubber stopper, through which

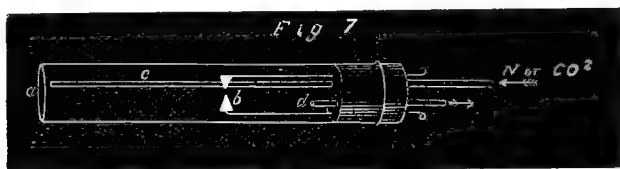


passed the tube of a globe funnel, with a stop-cock for the admission of the sulphuric acid, and an exit tube for the gas. The latter was plugged with asbestos to catch any liquid drops which might be thrown up, and was connected by a thick rubber tube to a tube of the form shewn in fig. 6. That part of this tube marked *a* was filled, one-half with soda-lime to catch acids, and the other half with phosphoric anhydride to catch moisture; the gas, after passing through this tube, was burnt as it issued from the narrow opening at *b*. The spectrum of the spark was observed through the small bulb blown on the end. The sulphuric acid was introduced gradually through the funnel, and the stream of gas allowed to pass through the tube for a long time. Sparks were passed between the wires, and the spectrum observed from time to time. At first the six violet bands were well seen, and the seven blue bands faintly; but gradually, as the air became more completely expelled, the blue bands disappeared entirely, and then the violet

bands so far died out that it was only by manipulating the coil that they could be made visible, and then only very faintly indeed. A bubble of air, estimated by the length of the tube it filled to be about $\frac{1}{400}$ of the volume of gas in the flask and tube, was now introduced through the funnel, and almost immediately the bands reappeared brightly. As the stream of gas however continued, they again gradually died away until they were represented only by a faint haze. It was subsequently found that each introduction of fresh acid into the flask was attended with a marked increase in the brightness of the nitrocarbon bands, which died away again when the current of gas was continued without fresh introduction of acid. On testing the acid it was found to contain, as is frequently the case with sulphuric acid, a small quantity of oxides of nitrogen. This quantity was, however, so small that the amount of nitrogen introduced at each introduction of acid must have been but a small portion of the amount introduced in the bubble of air above-mentioned, yet it gave a very sensible increase in the brightness of the nitrocarbon bands. The difficulty of getting all the air expelled from the apparatus led us next to adopt a modification of this experiment. The carbonic oxide was generated by heating, in a tube of hard glass in an ordinary combustion furnace, a mixture of pure and dry potassium oxalate with one quarter of its weight of quicklime, the mixture having been previously heated for some time so as to expel traces of ammonia. The rest of the apparatus was similar to that used in the previous experiment, but in order to expedite the removal of the air the narrow tube, *b*, was connected with a Sprengel pump, and the air exhausted before heating the oxalate. The distant end of the tube with the oxalate was then heated, and the whole apparatus filled with carbonic oxide; it was then again exhausted with the pump, refilled by heating more oxalate, and the gas allowed to stream out through the pump for some time. The heat was then lowered, sparks were passed and the spectrum observed. No trace whatever of the nitrocarbon bands could be detected, however the spark might be varied. The pump was now set going again, and the pressure of the gas reduced to 1 inch of mercury, while the spectrum was observed from time to time. Still no trace of the nitrocarbon bands could be detected. More of the oxalate was next heated, and the observations repeated again and again, always with the same result. We came, therefore, to the conclusion that carbonic oxide, if quite free from nitrogen, does not give, at the atmospheric or any less pressure, the nitrocarbon spectrum.

From Dr Watts' account of his experiments, it appeared that he had used carbonic oxide prepared by the action of sulphuric acid on ferrocyanide, and it was probable that it might have been contaminated with nitrogen, or with nitrogenous compounds, from the ferrocyanide. We accordingly repeated our experiments with carbonic oxide so prepared, and found that the nitrocarbon bands were then always distinctly seen.

We have also repeated Ångström and Thalén's experiments with the spark between carbon poles in nitrogen and carbonic acid gas. For this we used a wide glass tube (fig. 7), to one end of which a quartz lens, *a*, was cemented, while the other was stopped with a cork, through which were passed two stout platinum wires with little cones of carbon (*b*), purified in Bunsen's manner, fastened, as shewn in the figure, on to their ends. Two narrow glass tubes were also passed through the cork, one reaching the whole length of the bigger tube for the introduction of gas, and the other a short one for exit. The tube was first filled with nitrogen. On passing the spark we observed, as Ångström and Thalén say, that about the poles the nitrocarbon bands were plainly seen; and they were visible through a great range of variations of the character of the spark; even the use of a condenser of moderate size (a litre flask full of sulphuric acid and coated to the neck with tinfoil) did not diminish them. Photographs were then taken, with



and without the use of the condenser, and these shewed the violet and ultra-violet nitrocarbon bands including those near N and P. The nitrogen was now swept out by a current of carbonic acid gas, and on now passing the spark the nitrocarbon bands could no longer be detected, and photographs taken as before shewed no trace of any of them.

In order further to test the sensibility of the spectroscopic test for nitrocarbon compounds, and the permanence of such compounds under variations in the electric discharge, we drew out, so as to form long narrow necks, both ends of a glass tube of 110 cub. centims. capacity which had wires sealed into it in the same way as before, and into one of these necks we introduced a minute quantity, .002 grm., of mercury cyanide; a current of hydrogen was then passed through the tube at atmospheric pressure, and when it was judged that the air must be thoroughly expelled, the tube was closed by the blowpipe. On passing the spark no trace of nitrocarbon bands could be seen. The mercury cyanide was then heated to decomposition by a spirit lamp. The nitrocarbon bands immediately made their appearance, and were well, even brightly, seen, and they did not disappear when a strong spark from a very powerful induction-coil was passed, or even with the use of a condenser consisting of two such flasks as are above mentioned. There was no sign of any permanent decomposition of the cyanogen; the bands continued to shew well after the passage of the spark had been maintained for a long time. The whole quantity of cyanogen which the amount of cyanide introduced would give if it were wholly decomposed, which is not the case at the

temperature employed, is less than $\frac{1}{600}$ of the volume of the whole tube, *i.e.* of the hydrogen with which it was mixed.

It appears from this experiment not only that the test is an extremely sensitive one for nitrocarbon compounds, but that cyanogen is far more permanent under the electric discharge when mixed with a large bulk of hydrogen than when the discharge is passed through cyanogen alone.

In all the foregoing experiments the bands which Ångström and Thalén ascribe to hydrocarbons were always more or less plainly seen; and we have come to the conclusion that much more care than has generally been thought necessary is needed, if the last traces of hydrogen and its compounds are to be removed from spectral tubes. Indeed, we do not think that all water can be removed from apparatus and reagents which do not admit of being heated to redness. To illustrate this, we may mention one or two experiments.

Into the bulb of a sparking tube similar in form to that of fig. 4, but rather longer, some loose phosphoric anhydride was introduced and then some well dried and redistilled carbon bisulphide. The end of the tube having then been drawn out the carbon bisulphide was boiled out in an oil-bath at a temperature of 200° C., and the tube sealed off. On passing the spark without condenser the hydrocarbon bands were discernible, and on putting on the condenser the hydrogen line C came out plainly, and was identified by comparison with an ordinary vacuum tube containing hydrogen. One would have supposed that the phosphoric anhydride would have retained all the moisture, and that there could be no other source of hydrogen in the tube.

In another experiment a mixture of carbonate of sodium and boric anhydride, previously to admixture heated red hot, was introduced into one end of a piece of combustion tube, near the other end of which wires had been sealed, and the open end drawn out; the mixture was then heated, and when it was judged that all the air was expelled, the tube was sealed off at atmospheric pressure. On passing sparks through it carbonic oxide bands and oxygen lines could be seen, but no hydrogen, hydrocarbon, or nitrocarbon bands could be detected. It appears, therefore, that the application of a red heat is likely to prove a more effectual means of getting rid of moisture than the use of any desiccating agent.

The first point we have had before us in these investigations is whether the groups of shaded bands seen in the more refrangible part of the spectrum of a cyanogen flame, of which the three which can be detected by the eye are defined by us in our previous paper on this subject by their wave-lengths (4600 to 4502, 4220 to 4158, and 3883 to 3850), are due to the vapour of carbon uncombined, or, as we conclude, to a compound of carbon with nitrogen.

Now, the evidence that carbon uncombined can take the state of vapour at the temperature of the electric arc is at present very imperfect. Carbon shews at such temperatures only incipient fusion, if so much as that; and

that carbon uncombined should be vaporised at the far lower temperature of the flame of cyanogen is so incredible an hypothesis that it ought not to be accepted if the phenomena admit of any other probable explanation. On the other hand, we have shewn that cyanogen or hydrocyanic acid is generated in large quantity in the electric arc taken in nitrogen, and Berthelot has shewn that hydrocyanic acid is produced by the spark discharge in a mixture of acetylene and nitrogen, so that in the cases in which these bands shine out with the greatest brilliance, namely, the arc in nitrogen and the cyanogen flame, we know that nitrocarbon compounds are present. Further, we have shewn that these bands fade and disappear in proportion as nitrogen is removed from the arc. Ångström and Thalén had previously shewn the same thing with regard to the discharge between carbon electrodes; and the conclusion to which they and we have come would probably have commanded universal assent if it had not been for the fact that these bands had been seen in circumstances where nitrogen was supposed to be absent; but where, in reality, the difficulty of completely eliminating nitrogen, and the extreme sensibility of the spectroscopic test, had been inadequately apprehended.

To clear up the question from this point of view, the experiments now detailed have been made, and they appear to us quite conclusive. Were the evidence less conclusive than it is, it would still be as rash and as illogical to conclude from the appearance of the nitrocarbon bands in a case where nitrogen was presumed, not proved, to be absent, that they were not due to a nitrocarbon, as it would be to deny that the well-known yellow lines were due to sodium, because they had been seen in cases where sodium was supposed to be absent. Our argument is an induction from a very long series of observations which lead up to one conclusion, and hardly admit of any other explanation. But Mr Lockyer attempts to explain the disappearance of the bands when nitrogen is absent, by the statement "that the tension of the current used now brings one set of flutings into prominence, and now another." This is no new observation. It is well known that variations in the discharge produce variations in the relative intensities of different parts of a spectrum. Certain lines of magnesium, cadmium, zinc, and other metals, very brilliant in the spark, are not seen, or are barely seen, at all in the arc. His remark might be applied to the spectra of compounds as well as to those of elements. Variation in the discharge accounts very well for some of the variations of intensity in the bands if they be due to a nitrocarbon; it will not, however, account for the fact observed by us, that the bands, or those of them which have the greatest emissive power, and are best developed by the particular current used, come out on the addition of a minute quantity of nitrogen, when there is every reason to think that no variation of the current occurs*.

* It is worthy of note, that if we number the sets of bands of the spectrum of hydrocarbons, beginning with the orange set, and those of cyanogen, beginning with the least refrangible of

Much the same may be said with regard to the changes of the spectrum produced by changes of temperature. We cannot infer from any of these changes that the spectrum is not due to a compound. The bands in question are singularly persistent through a great range of temperatures, from the temperature of a cyanogen flame cooled by admixture with carbonic acid gas, as related by Watts (*Phil. Mag.*, 1869, p. 258), to that of the spark of an induction-coil with condenser.

But again, Mr Lockyer attempts to get over the difficulties of his case by the supposition that "the sets of carbon flutings represent different molecular groupings of carbon, in addition to that or those which give us the line spectrum."

Now, until independent evidence that carbon can exist at all in the state of vapour uncombined at the temperature of a cyanogen flame can be adduced, and further independent evidence of the existence of different groupings in such vapour, the hypothesis here enunciated is a gratuitous one, so long as any other hypothesis for which independent evidence can be adduced, as is true of the existence of nitrocarbon compounds in the flame, arc, and spark, will sufficiently explain the facts.

Whether or no the nitrocarbon bands are visible in the solar spectrum is not in dispute, for we have never hitherto expressed any opinion on that point. The observation above recorded, that there is in the spectrum of cyanogen a strong shaded band coincident with the very characteristic dark shaded band P, strengthens materially the evidence in favour of the existence of these bands in the solar spectrum; the more so, as the series of lines at P has far more of the distinctive character of the cyanogen spectrum than any other series in the ultra-violet part of the solar spectrum.

However that may be, we contend against the hypothesis that if present they can be due to any vapour of carbon uncombined in the upper cooler region of the chromosphere. One object of our investigations has been to determine the permanence of compounds of non-metallic elements, and the sensitiveness of the spectroscopic test in regard to them. It appeared probable that if such compounds existed in the solar atmosphere their presence would be most distinctly revealed in the more refrangible part of the spectrum, and this is a subject with which we purpose to deal in a further communication. In the meantime it is sufficiently clear that the presence of nitrogen in the solar atmosphere may be recognised through cyanogen when free nitrogen might escape detection.

In a footnote of his paper Mr Lockyer assigns the wave-length 3881 as

those shewn in our diagram, fig. 1, then the most persistent in the hydrocarbon flame-spectrum are 3 and 5, while in the visible part of the spectrum of cyanogen they are 3 and 4, but there are conditions of the nitrocarbon spectrum in which the three lines near G seem to be most persistent.

approximately that of the least refrangible edge of the ultra-violet set of bands next above K, whereas in our former paper we had given it as 3883·5. Now, as we have before explained, we have never set ourselves to the exact determination of wave-lengths, we have rather used them as convenient handles by which to designate particular lines; but a repetition of the measures of our photographs does not confirm Mr Lockyer's number. The photographs were those of the arc from a De Meritens machine in one of our lime crucibles, and gave the iron lines well developed; and we used the iron lines, wave-lengths 3906, 3902, 3898·5, 3894·8, and the pair between 3877 and 3878 as lines of reference. These measures give, as a minimum, the wave-length 3882·7. In Cornu's map a manganese line is given with the wave-length 3881. None of our photographs shew this line, though manganese was purposely introduced into the crucible, and the other manganese lines came out well and strong. We should not put a determination made in this way against a direct determination of the wave-length by a diffraction grating; but unless there be an error in the identification of the iron lines, or Cornu's wave-lengths for those lines be erroneous, neither of which suppositions is at all probable, we conclude that the wave-length is more nearly 3883 than 3881. If this be correct, the band covers a markedly luminous portion of the solar spectrum as shewn in Cornu's map.

Mr Lockyer has forced us to go again over some of the ground which we had previously traversed, by making such a statement as the following:—

“I have therefore thought it desirable to go over the ground again, modifying the experimental method so as to demonstrate the absence of impurities. Indeed, I have started upon a somewhat lengthy research, and have taken a large number of photographs under various conditions, so that to reduce them all will be a work of time. I beg permission, therefore, in the meantime, to submit to the notice of the Society an experiment with a tube containing CCl_4 , which, I think, establishes the conclusions arrived at by prior investigators. And I may add that it is the more important to settle the question, as Messrs Liveing and Dewar have already based upon their conclusions theoretical views of a kind which appear to me calculated to mislead, and which I consider to have long been shewn to be erroneous.”

As we have now demonstrated the utterly unsatisfactory character of the crucial experiment on the strength of which Mr Lockyer condemns in so sweeping a manner our conclusions, it is unnecessary to add any further comment*.

* Mr Lockyer has communicated to the Society a “Further Note on the Spectrum of Carbon” since the above was written. We see no reason to modify our conclusions regarding the carbon spectrum on account of any new facts brought forward. The discussion of the paper we leave until a future occasion.

ON THE SPECTRUM OF WATER

[*Proceedings of the Royal Society*, Vol. xxx. (1880), pp. 580 sqq.]

IN our last communication to the Society, "On the Spectra of the Compounds of Carbon with Hydrogen and Nitrogen, No. II," we noticed that a remarkable series of lines, extending over the region between the lines S and R of the solar spectrum, was developed in the flame of coal-gas burning in oxygen. The arrangement of lines and bands, of which this spectrum consists, is shewn in the accompanying diagram*, fig. 1. It begins at the more refrangible end with two strong bands, with wave-lengths about



FIG. 1.

3062, 3068, and extends up to about the wave-length 3210. It is well developed in the flame of hydrogen as well as of hydrocarbons, burning in oxygen, and less strongly in the flames of non-hydrogenous gases, such as carbonic oxide and cyanogen, if burnt in moist oxygen. Special pains were taken to purify the gases from sulphur. The same spectrum is given by the electric spark taken, without condenser, in moist hydrogen, oxygen, nitrogen, and carbonic acid gas, but it disappears if the gas and apparatus be thoroughly dried. We are led to the conclusion that the spectrum is that of water. The accompanying diagram, fig. 2, shews the apparatus used for comparing the spectra of the spark in the gases, dry and moist. The tube in which the sparks were passed was closed at the end *b* by a quartz lens cemented to the

* This diagram gives tolerably well the general character of the spectrum, but the artist has not in all cases correctly rendered the relative strength of the lines. Those of the less refrangible half are almost too strongly rendered.

glass; *c c* were platinum wires sealed into the glass. The gas was introduced through the narrow tube *a*, provided with a branch closed by a glass stopcock. The gas was passed from the gas-holder through two long drying-tubes, of which the first was filled with calcium chloride, and the second with phosphoric anhydride. The joints were all made with dry corks, in order to avoid the hydrocarbons which contaminate gases passed through rubber tubes. The exit-tube *d* was armed with a tube of phosphoric anhydride, to prevent moisture entering that way. It was necessary to pass a current of dry gas for fully an hour through the warmed apparatus before the moisture was sufficiently expelled. When this was done, photographs of the spark shewed either no trace, or only the faintest traces, of the spectrum above described. On now introducing a drop of water through the stopcock in the branch at *a*, and letting it spread over a plug of asbestos placed in the tube at *a*, the current of gas of course passed into the sparking tube moist instead of dry; and on now passing the spark, the spectrum above described at once

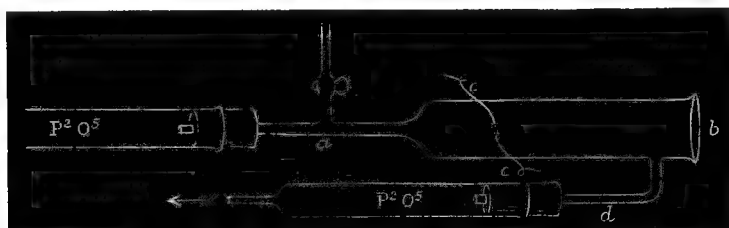


FIG. 2.

imprinted itself on the photographic plate. The effect was the same, whether the gas used were hydrogen, oxygen, nitrogen, or carbonic acid. In the case of nitrogen, some of the channelled bands due to that gas overlap the water spectrum, and partly obscure it, but not so much but that it can be still very distinctly recognised. When a condenser is used, the water spectrum disappears. The same spectrum seems to appear in the De Meritens arc, but is much less fully developed. The spectrum we have figured does not by any means exhaust the ultra-violet spectra of the flames we have observed, but it is as much as we have been able at present to observe closely and to trace to water as its cause. In writing of this and other spectra which we have traced to be due to compounds, we abstain from speculating upon the particular molecular condition or stage of combination or decomposition, which may give rise to such spectra. The interest of finding an ultra-violet spectrum of water in a flame at all seemed to justify our laying before the Society so much as we have already determined. It opens up questions as to the emissive power for radiation of short wave-length of gaseous substances at the comparatively low temperatures of flames, with regard to which we

are accumulating facts, which we propose to discuss in a future communication. It is obvious, however, that this opens up a very large and extensive field of inquiry which will necessitate great precautions in the conduct of the experiments; for instance, we are not prepared to guarantee that oxides of nitrogen from traces of air may not have something to do with some parts of the spectrum here described. Such facts as we have placed before the Society will completely modify the inferences which have been drawn as to the assumed continuity of flame spectra even under compression, and as to the character of the specific absorption of the vapour of water.

INVESTIGATIONS ON THE SPECTRUM OF MAGNESIUM

[*Proceedings of the Royal Society*, Vol. XXXII. (1881), pp. 189 sqq.]

SINCE our last communication on this subject (*supra*, p. 78) several authors—Ciamician, Cornu and Fievez—have published observations on the spectrum of magnesium, to some of which allusion is made in the sequel, but these observations by no means exhaust the subject. Our own observations, carried on for a considerable time, have extended to new regions and a variety of circumstances, and the summary of them which we now present to the Society will, we hope, help to bring out the connexion between some of the variations in the spectrum of this element and the conditions under which it is observed, and throw additional light on the question of the emissive power for radiations of short wave-length of substances at the relatively low temperature of flame to which we alluded in our paper on the spectrum of water (*supra*, p. 115).

We begin with an account of these observations.

Spectrum of the Flame of Burning Magnesium.

When magnesium wire or ribbon is burnt in air, we see the three lines of the *b* group, the blue line about wave-length 4570, first noticed by us in the spark spectrum (*supra*, p. 14); and photographs shew, besides, the well-known triplet in the ultra-violet between the solar lines K and L sharply defined, and the line for which Cornu has found the wave-length 2850 very much expanded and strongly reversed. These lines are all common to the flame, arc, and spark spectra; and the last of them (2850) seems to be by far the strongest line both in the flame and arc, and is one of the strongest in the spark. But, in addition to these lines, the photographs of the flame shew a very strong, somewhat diffuse, triplet, generally resembling the other magnesium triplets in the relative position of its components, close to the solar line M; and a group of bands below it extending beyond the triplet near L. These bands have, for the most part, each one sharply defined edge, but fade away on the other side; but the diffuse edges are not all turned towards the same side of the spectrum. The positions of the sharp edges of these bands, and of the strong triplet near M, are shewn in the

figure, No. 1. It is remarkable that the triplets near P and S are absent from the flame spectrum, and that the strong triplet near M is not represented at all either in the arc or spark. The hydrogen-magnesium series of lines, beginning at a wave-length about 5210, are also seen sometimes, as already described by us (*supra*, p. 80), in the spectrum of the flame; but we have never observed that the appearance of these lines, or of the strong line with which they begin, is connected with the non-appearance of b_4 . Indeed, we can almost always see all three lines of the b group in the flame, though as b_4 is the least strong of the three, it is likely to be most easily overpowered by the continuous spectrum of the flame. The new observations recorded below leave, we think, no room for doubt that the series of lines beginning at wave-length 5210 are due to a combination of hydrogen with magnesium, and are not dependent solely on the temperature.

The wave-lengths of the strong triplet near M are about 3720, 3724, 3730, and of the defined edges of the bands about 3750, 3756, 3765, 3772, 3777, 3782, 3790, 3799, 3806, 3810, 3815, 3824, 3841, 3845, 3848, 3855, 3858, 3860, 3865.

Burning magnesium in oxygen instead of atmospheric air does not bring out any additional lines; on the contrary, the continuous spectrum from the magnesia overpowers the line spectrum, and makes it more difficult of observation.

Magnesia heated in the oxy-hydrogen jet does not appear to give the lines seen in the flame.

We have left out of the figure and from the enumeration of lines the well-known bands of the oxide.

Spectrum of the Arc.

By examining the arc of a battery of 40 Grove's cells, or that of a Siemens machine, taken in a crucible of lime, under the dispersion of the spectrum of the fourth order given by a Rutherford grating of 17,296 lines to the inch, we are able to separate the iron and magnesium lines which form the very close pair b_4 of the solar spectrum. Either of the two lines can be rendered the more prominent of the pair at will, by introducing iron or magnesium into the crucible. The less refrangible line of the pair is thus seen to be due to iron, the more refrangible to magnesium. Comparison of the solar line and the spark between magnesium points confirms this conclusion, that the magnesium line is the more refrangible of the two.

In the ultra-violet part of the spectrum photographs shew several new lines. First, a pair of lines above U at wave-lengths about 2942, 2938.5*.

* [Many of our photographs shew besides these two lines a third line wave-length about 2937.5, but we have not been able to determine certainly that it is due to magnesium. If so this group probably belongs to the series of triplets. June 2.]

These lines are a little below a pair of lines given by the spark for which Cornu has found the wave-lengths 2934·9, 2926·7. The latter pair are not seen at all in photographs of the arc, nor the former in those of the spark. The strong line, wave-length about 2850, is always seen, very frequently reversed. Of the quadruple group in the spark to which Cornu has assigned the wave-lengths 2801·3, 2797·1, 2794·5, and 2789·9, the first and third are strongly developed in the arc, the other two not at all. Next follows a set of five nearly equidistant lines, well-defined and strong, but much less strong than the two previously mentioned, wave-lengths about 2782·2, 2780·7, 2779·5, 2778·2, 2776·9. The middle line is a little stronger than the others. The same lines come out in the spark.

Beyond these follow a series of pairs and triplets; probably they are triplets in every case, but the third, most refrangible, line of the triplets is the weakest, and has not in every case been noticed as yet. These succeed one another at decreasing intervals with diminishing strength, and are alternately sharp and diffuse, the diffuse triplets being the strongest. The positions are shewn in fig. 2. The series resembles in general character the sodium and the potassium series described by us in a former communication, and we cannot resist the inference that they must be harmonically related, though they do not follow a simple harmonic law. The most refrangible line in the figure at wave-length 2605 represents a faint diffuse band which is not resolvable into lines; it belongs, no doubt, to the diffuse members of the series, and, to complete the series, there should be another sharp group between it and the line at wave-length 2630. This belonging to the weaker members of the series is too weak to be seen.

The approximate wave-lengths found by us for these lines are as follows:—2767·5, 2764·5, 2736, 2732·5, 2731, 2698, 2695, 2693·5, 2672·5, 2670, 2668·5, 2649, 2646, 2633, 2630, 2605.

It is worthy of remark that the line at wave-length 5710, described by us in a previous communication (*supra*, p. 82), is very nearly the octave of the strong line at 2850. Moreover the measures we have taken of the wave-length of this last line, with a Rutherford grating of 17,296 lines to the inch, indicate a wave-length 2852 nearly, which is still closer to the half of 5710.

In Cornu's map of the solar spectrum a line is ascribed to magnesium with the wave-length 3278. Although a line at this place appears in many of our photographs of the arc, we have not been able to identify it as a line due to magnesium. It does not shew any increased strength when magnesium is introduced into the arc. When metallic magnesium is dropped into a crucible of magnesia or lime through which the arc is passing, the electric current seems sometimes to be conducted chiefly or entirely by the vaporised metal, so that the lines of other metals almost or wholly disappear;

but the line at wave-length 3278 does not in such cases appear, though the other magnesium lines are very strongly developed. The line at wave-length 2850 is often, under such circumstances, enormously expanded and reversed, those at wave-lengths 2801, 2974, and the alternate diffuse triplets, including those near L and near S, much expanded and reversed, and the group of five lines (2776—2782) sometimes reversed.

When the arc of a Siemens machine is taken in a magnesia crucible, the strong line of the flame spectrum, wave-length 4570, is well seen sharply defined; it comes out strongly and a little expanded on dropping in a fragment of magnesium. When a gentle stream of hydrogen is led in through a hollow pole, this line is frequently reversed as a sharp black line on a continuous background. From comparing the position of this line with those of the titanium lines in its neighbourhood, produced by putting some titanite oxide into the crucible, we have little doubt that it is identical with the solar line 4570.9 of Ångström.

When the arc is taken in a crucible into which the air has access, it may be assumed that the atmosphere about the arc is a mixture of nitrogen and carbonic oxide. When a stream of hydrogen is passed, either through a perforated pole or by a separate opening, into the crucible, the general effect is to shorten the length to which the arc can be drawn out, increase the relative intensity of the continuous spectrum, and diminish the intensity of the metallic lines. Thus, with a very gentle stream of hydrogen in a magnesia crucible, most of the metallic lines, except the strongest and those of magnesium, disappear. Those lines which remain are sometimes reversed; those at wave-length 2850 and the triplet near L being always so. With a stronger stream the lines of magnesium also disappear, the *b* triplet being the last in that neighbourhood to go, and *b*₁ and *b*₂ remaining after *b*₃ has disappeared.

Chlorine seems to have an opposite effect to hydrogen, generally intensifying the metallic lines, at least those of the less volatile metals, but it does not sensibly affect the spectrum of magnesium. Nitrous oxide produces no marked effect; coal-gas acts much as hydrogen.

Spectrum of the Spark.

In the spark of an induction-coil taken between magnesium points in air we get all the lines seen in the arc except two lines at wave-lengths 4350 and 4166, two lines above U, and the series of triplets more refrangible than the quintuple group about wave-length 2780. The blue line wave-length about 4570 is seen in the spark without a jar when the magnesium electrodes are close together, and the rheotome made to work slowly, but requires for its detection a spectroscope in which the loss of light is small.

On the other hand, some additional lines are seen. Of these, the strong line at wave-length 4481 and the weak line at 4586 are well known.

Another faint line in the blue at wave-length 4808* has been observed by us in the spark, and two diffuse pairs between H and the triplet near L. Two ultra-violet lines at wave-lengths 2934·9, 2926·7 (Cornu) are near, but not identical with, two lines of the arc above-mentioned; and two more lines at wave-lengths 2797·1, 2789·9 (Cornu) make a quadruple group with the very strong pair which are conspicuous in the arc in this region. The spectrum of the spark ends, so far as we have observed, with the quintuple group (2782—2776) already described in the arc. The lines of this spectrum are given in fig. 3.

When a Leyden jar is used with the coil, some of the lines are reversed. This is notably the case with the triplet near L, the line at wave-length 2850, and those at 2801 and 2794. Cornu (*Compt. Rend.*, 1871) noticed the reversal of the less refrangible two lines of the triplet near L under these circumstances. This effect is very much increased by increasing the pressure of the gas in which the spark is taken. For the purpose of observing the influence of increased pressures, we have used a Cailletet pump and glass tubes similar to those employed in the liquefaction of gases by means of such a pump, but with an expansion of the upper part in which were magnesium electrodes attached to platinum wires sealed into the glass. The tube having been filled with gas at the atmospheric pressure, was sealed at its upper end, while the lower end dipped into mercury contained in the iron bottle of the Cailletet pump, and the gas was afterwards compressed by driving more or less mercury into the tube. The gases used were hydrogen, nitrogen, and carbonic oxide; and the image of the spark was thrown on to the slit of the spectroscope by a lens. In hydrogen, when no Leyden jar was used, the brightness of the yellow and of the blue lines of magnesium, except at first that at wave-length 4570, diminished as the pressure increased; while, on the other hand, the *b* group was decidedly stronger at the higher pressure. The pressure was carried up to 20 atmospheres, and then the magnesium lines in the blue and below, almost or entirely, disappeared, leaving only the *b* group very bright, and the magnesium-hydrogen bands which are described below; even the hydrogen lines F and C were not visible. When a jar was used, the magnesium lines expanded as the pressure was increased; all three lines of the *b* group were expanded and reversed at a pressure of 5 atmospheres; the yellow line, wave-length 5528, was also expanded but not reversed; and the line at 4481 became a broad, very diffuse band, but the line at wave-length 4570 was but very little expanded. The expansion both of the *b* group and of the yellow line seemed to be greater on the less refrangible than on the more refrangible side of each line, so that the black line in those which were reversed was not in the middle. When the jar was

* This line we first noticed in a former communication (*supra*, p. 14), but the wave-length is there given, through an error in taking out the ordinate of the curve of interpolation, as 4797 instead of 4807. Another measure has given the wave-length 4808.

used the pressure could not be carried beyond 10 or $12\frac{1}{2}$ atmospheres, as the resistance became then so great that the spark would not pass across the small distance of about 1 millim. between the electrodes. At a pressure of $2\frac{1}{2}$ atmospheres, with a jar, the ultra-violet magnesium triplet near L was very well reversed, and the two pairs of lines on its less refrangible side (shewn in fig. 3) were expanded into two diffuse bands.

In nitrogen and in carbonic oxide the general effects of increased pressure on the magnesium lines (not the magnesium-hydrogen bands) seemed to be much the same as in hydrogen. Without a jar the blue and yellow lines were enfeebled, and at the higher pressures disappeared, while the *b* group was very brilliant but not much expanded. With the jar all the lines were expanded, and all three lines of the *b* group strongly reversed. The bands of the oxide (wave-length 4930—5000) were not seen at all in hydrogen or nitrogen; they were seen at first in carbonic oxide, but not after the sparking had been continued for some time,

The disappearance of certain lines at increased pressure is in harmony with the observations of Cazin (*Phil. Mag.*, 1877, Vol. iv, p. 154), who noticed that the banded spectrum of nitrogen, and also the lines, grew fainter as the pressure was increased, and finally disappeared. When a Leyden jar is employed there is a very great increase in the amount of matter volatilized by the spark from the electrodes, as is shewn by the very rapid blackening of the sides of the tube with the deposited metal, and this increase in the amount of metallic vapour may reasonably be supposed to affect the character of the discharge, and conduce to the widening of the lines and the reversal of some of them. Without a jar the amount of matter carried off the electrode also doubtless increases with the pressure and consequent resistance, and may be the cause of the weakening, as Cazin suggests, of the lines of the gas in which the discharge is passed. It is to be noted, moreover, that the disappearance of the hydrogen lines depends, in some degree, on the nearness of the electrodes. The lines C and F which were, as above stated, sometimes invisible in the spark when the electrodes were near, became visible, under circumstances otherwise similar, when the magnesium points had become worn away by the discharge.

M. Ch. Fievez (*Bull. de l'Académie Royale de Belgique*, 1880, p. 97) has investigated the variations in the appearance of the spark spectrum of magnesium under certain different conditions. Using a Rutherford grating of 17,296 lines to the inch, he has noticed certain lines about the *b* group which increase in number with the order of the spectrum observed. He has also noticed dark lines in the solar spectrum corresponding to these lines of magnesium when the two spectra were superposed (fig. 5). We have noticed similar lines in the spectrum of magnesium given by a Rutherford grating, but attribute them to a different cause. The Rutherford gratings have a

periodic inequality in the ruling, due to an imperfection of the screw of the ruling machine, in consequence of which the image of every bright line is accompanied by a series of fainter images at nearly equal distances on either side of it, diminishing rapidly in brightness as they recede from the principal line. These *ghosts* are so much fainter than the principal lines that they are not noticed in the case of any but bright lines, and except in the case of very bright lines only two, one on each side, are seen to accompany each principal line.

Solar spectrum by
Rutherford grat-
ing, 4th order, after
M. Fievez

Magnesium

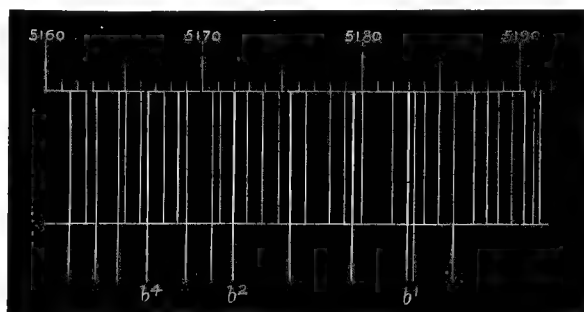
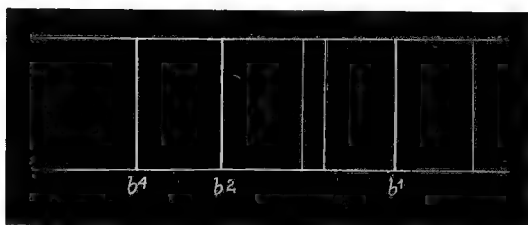


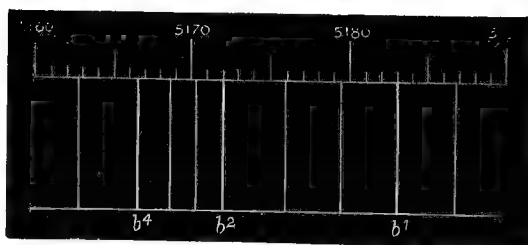
FIG. 5.



Spectrum of
3rd order

FIG. 6.

Magnesium *b*
group with
ghosts pro-
duced by
Rutherford
grating



Spectrum of
4th order

FIG. 7.

The positions of these *ghosts* have been investigated by Mr Peirce in the *Mathematical Journal* of the Johns Hopkins University, Baltimore, who has found theoretically, and confirmed it by actual observation, that the distance between successive images of the same line is directly proportional to the dispersion and inversely as the order of the spectrum. Our own observations of the positions of the *ghosts* of the *b* group of magnesium lines in spectra of

different orders agree closely with Mr Peirce's theory, and two different Rutherford gratings both give us the same results. The annexed diagrams (figs. 6 and 7) give the relative positions of the first pair of *ghosts* of each of the lines of the *b* group in the spectra of the third and fourth orders, when the angle between collimator and telescope is 45° . If this is compared with M. Ch. Fievez's map, it will be seen that he has probably been deceived by these *ghosts*, both in the solar spectrum and in that of the spark; but as he does not state the angle between his collimator and telescope, no exact comparison can be made. These ghosts are sometimes very embarrassing when many lines are in the field of view, but they may be detected by comparing the spectra of different orders, as the ghosts have different relative positions in the spectra of different orders. In the spectrum of the third order the first ghost of b_2 on the more refrangible side falls on b_4 , and that of b_4 on its less refrangible side falls on b_2 .

The Magnesium-hydrogen Spectrum.

In the *Proc. Roy. Soc.*, Vol. xxvii, p. 494, and Vol. xxx, p. 93*, we have recorded a series of experiments which led us to attribute to magnesium together with hydrogen a peculiar spectrum. This spectrum we have on no occasion been able to detect in the absence of hydrogen. Observations on the spark discharge in nitrogen, in carbonic oxide, and in hydrogen, at reduced pressures, confirmed the results given in the first-mentioned paper, when the discharge was taken in the gases at atmospheric pressure. It was further shewn that this peculiar spectrum could be reversed during the voltaic discharge in a lime crucible, provided magnesium and hydrogen were both present, but not in the absence of hydrogen. Likewise the flame of burning magnesium was found to emit this spectrum when the combustion occurred in an atmosphere containing either free or combined hydrogen. In summing up our results the following opinion was expressed:—

“The experiments above described, with nitrogen and carbonic oxide at reduced pressures, are almost, if not quite, conclusive against the supposition that the line at 5210 is due merely to the lower temperature of the spark in hydrogen. From De La Rue and Müller's observations it would appear that nitrogen at a pressure of 400 millims. should produce much the same effect on the spark as hydrogen at 760 millims. Now the pressures of the nitrogen and carbonic oxide were reduced far below this without any trace of the line in question being visible. Moreover, the magnesium line at 4481, which is not seen in the arc, and may be reasonably ascribed to the higher temperature of the spark, may be seen in the spark at the same time as the line at 5210 when hydrogen is present. Nevertheless, temperature does seem to affect the result in some degree, for when a large Leyden jar is used, and the gas is at the atmospheric pressure, the line almost disappears from the spark,

* *Supra*, pp. 16 and 78.

to reappear when the pressure is reduced; but by no variation of temperature have we been able to see the line when hydrogen was carefully excluded.

"A line of the same wave-length has been seen by Young in the chromosphere once. Its absence from the Fraunhofer lines leads to the inference that the temperature of the sun is too high (unless at special times and places) for its production. If it be not due to a compound of magnesium with hydrogen, at any rate it occurs with special facility in the presence of hydrogen, and ought to occur in the sun if the temperature were not too high.

"We have been careful to ascribe this line and its attendant series to a mixture of magnesium and hydrogen rather than to a chemical compound, because this expresses the facts, and we have not yet obtained any independent evidence of the existence of any chemical compound of those elements."

Fig. 4 shews more completely than we have given it before the general character of this spectrum, which consists of two sets of flutings and a pair of fainter bands, the flutings closely resembling in character the hydrocarbon flutings, each fluting consisting of a multitude of fine lines closely set on the less refrangible side and becoming wider apart and weaker towards the more refrangible side, but extending under favourable circumstances much further than is shewn in the figure. The set in the green is the stronger, and it was to this that our former observations were confined. It has two flutings, one beginning at about wave-length 5210 and the other close to b_1 on its more refrangible side. The other set consists of three principal flutings, of which the first begins at about wave-length 5618, the next at about wave-length 5566, and the third begins with three strong lines at about the wave-lengths 5513, 5512, 5511. Both sets are very well seen when a magnesium wire is burnt in the edge of a hydrogen flame, and in the arc in a crucible of magnesia when a gentle current of hydrogen is led into it. The less refrangible edges of the bands are at wave-lengths about 4849 and 4803.

As Mr Lockyer, in a paper entitled "A New Method of Spectrum Observation" (*Proc. Roy. Soc.*, Vol. xxx, p. 22), has brought forward this spectrum as illustrative and confirmatory of his views regarding the possibility of elemental dissociation at different heat-levels, we have been induced to review our former work. The view taken by Mr Lockyer may be expressed in his own words.

"The flame spectrum of magnesium perhaps presents us best with the beautiful effects produced by the passage from the lower to the higher heat-level, and shews the important bearing on solar physics of the results obtained by this new method of work.

"In the flame the two least refrangible of the components of b are seen

associated with a line less refrangible so as to form a triplet. A series of flutings and a line in the blue are also seen.

“On passing the spark all these but the two components of *b* are abolished. We get the wide triplet replaced by a narrow one of the same form, the two lines of *b* being common to both.....

“May we consider the existence of these molecular states as forming a true basis for Dalton’s law of multiple proportions? If so, then the metals in different chemical combinations will exist in different molecular groupings, and we shall be able by spectrum observations to determine the particular heat-level to which the molecular complexity of the solid metal, induced by chemical affinity, corresponds.

“*Examples.*—None of the lines of magnesium special to the flame spectrum are visible in the spectrum of the chloride either when a flame or a spark is employed.”

In order to ascertain if this spectrum could be produced at a high temperature in the presence of hydrogen, which element we have already shewn to be essential to its production at the atmospheric and at reduced pressures, the series of experiments already mentioned in describing the spark spectrum were made with hydrogen at pressures increasing up to twenty atmospheres.

On the supposition that this spectrum originates from the formation of some chemical compound, probably formed within certain limits of temperature when vapour of magnesium is in presence of hydrogen, the stability of the body ought to depend largely on the pressure of the gaseous medium. Like Graham’s hydrogenium, this body might be formed at a temperature at which it would under ordinary circumstances be decomposed, provided the pressure of the hydrogen were correspondingly increased. In fact, it has been shewn by Troost that the hydrides of palladium, sodium, and potassium all follow strictly the laws of chemical dissociation enunciated by Deville; and increased pressure by rendering the compound more stable, provided the secondary effect of such pressure in causing a higher temperature in the electric discharge were not overpowering, ought to conduce to a more continuous and brilliant spectrum of the compound. Conversely, if such a more continuous and brilliant spectrum be found to result, in spite of the higher temperature, from increased pressure, it can only be explained by the stability of the substance being increased with the pressure.

Now what are the facts? When the spark of an induction-coil, without a Leyden jar, is passed between magnesium electrodes in hydrogen at atmospheric pressure, the flutings in the green are, as before described, always seen, but they are much stronger at the poles and do not always extend quite across the field. As the pressure is increased, however, they increase in brilliance and soon extend persistently from pole to pole, and go on increasing

in intensity, until, at fifteen and twenty atmospheres, they are fully equal in brilliance to the *b* group, notwithstanding the increased brightness these have acquired by the higher temperature, due to the increased pressure. The second set of flutings, those in the yellowish-green, come out as the pressure is increased, and, in fact, at twenty atmospheres only the *b* group and the flutings are noticeable; if the yellow magnesium line be visible at all it is quite lost in the brilliance of the yellow flutings. The tail of fine lines of these flutings extends at the high pressure quite up to the green, and those of the green flutings quite up to the blue. On again letting down the pressure the like phenomena occur in the reverse order, but the brilliance of the flutings does not diminish so rapidly as it had increased. If, now, when the pressure has again reached that of the atmosphere, a large Leyden jar be interposed in the circuit, on passing the spark the flutings are still seen quite bright, and they continue to be seen with gradually diminishing intensity until the sparks have been continued for a considerable time. It appears that the compound, which had been formed in large quantity by the spark without jar at the higher pressures, is only gradually decomposed, and not re-formed, by the high temperature of the spark with jar. This experiment, which was several times repeated, is conclusive against the supposition that the flutings are merely due to a lower temperature. When the pressure was increased at the same time that the jar was employed, the flutings did not immediately disappear, but the expansion of the magnesium lines and the increase of the continuous spectrum seemed to overpower them.

When nitrogen was substituted for hydrogen, the strongest lines of the green flutings were seen when the spark without jar was first passed at atmospheric pressure, probably from hydrogen occluded, as it usually is, in the magnesium electrodes. As the pressure was increased they speedily disappeared entirely and were not again seen either at high or low pressures.

With carbonic oxide the same thing occurred as with nitrogen; but in this gas the flutings due to the oxide of magnesium (wave-length 4930 to 5000) were, for a time, very well seen.

Ciamician (*Sitzungsber. Akad. Wissensch.*, Wien, 1880, p. 437) has described a spectrum of magnesium of the first order (in Plücker's nomenclature) obtained by taking sparks from an induction-coil, without a jar, between magnesium electrodes in an atmosphere of hydrogen. He gives a figure to a scale of this spectrum, but it is not to a scale of wave-lengths, so that exact comparison of his observations with ours is difficult. The least refrangible set of flutings in his figure corresponds very well with that we have described in the yellowish-green. The next set, in the green, in his figure does not, however, correspond exactly with ours; it begins nearer to *b* than we have observed and consists of four flutings, whereas we observe but two in this set. It looks as if, in his figure, the magnesium-hydrogen

spectrum were superposed upon the hydrocarbon spectrum in this region. Further, he gives a third more refrangible set of flutings which we have only observed as two blue bands, not fluted. This third set of flutings, as drawn in his figure, appears to be somewhat more refrangible than the set due to the oxide, and occupies partly the place of the blue hydrocarbon series, but a passage in the text, in which he says that the magnesium spectrum of the second order might, without measurement, easily be taken to be identical with that of carbon, almost negatives the supposition that this set of flutings is the blue hydrocarbon set and mistaken for a magnesium spectrum of the first order. To whatever it may be due, we have not seen anything closely resembling it under the circumstances described by him, though our observations on the spark spectrum of magnesium in hydrogen have now been repeated with all the variations of circumstances which we could devise.

Mr Lockyer states (*loc. cit.*) that none of the lines of magnesium, special to the flame spectrum, are visible in the spectrum of the chloride, either when a flame or a spark is employed. But we find that when the spark is taken between platinum points from a solution of the chloride of magnesium, in a tube such as those used by Delachanal and Mermet, the line at wave-length 5210 can frequently be seen in it when the tube is filled with air, and that if the tube be filled with hydrogen the green flutings of magnesium-hydrogen are persistent and strong.

Repeated observations have confirmed our previous statements as to the facility with which the magnesium-hydrogen spectrum can be produced in the arc by the help of a current of the gas. In a magnesia crucible, by regulating the current of hydrogen, the flutings can be easily obtained either bright or reversed.

Comparison of the Spectra.

When we compare the spectra of magnesium in the flame, arc, and spark, we observe that the most persistent line is that at wave-length 2850, which is also the strongest in the flame and arc, and one of the strongest in the spark. The intensity of the radiation of magnesium at this wave-length is witnessed by the fact that this line is always reversed in the flame as well as in the arc when metallic magnesium is introduced into it, and in the spark between magnesium electrodes when a Leyden jar is used. It is equally remarkable for its power of expansion. In the flame it is a broad band, and equally so in the arc when magnesium is freshly introduced, but fines down to a narrow line as the metal evaporates.

Almost equal in persistence are the series of triplets. Only the least refrangible pair of these triplets is seen in the flame, another pair is seen in the spark, but the complete series is only seen in the arc. We regard the

triplets as a series of harmonics, and to account for the whole series being seen only in the arc we must look to some other cause than the temperature. This will probably be found in the greater mass of the incandescent matter contained in the crucible in which the arc was observed.

The blue line of the flame at wave-length 4570 is well seen in the arc, and is easily reversed, but is always a sharp line, increased in brightness but not sensibly expanded by putting magnesium into the crucible. In the spark, at atmospheric pressure, it is only seen close to the pole or crossing the field in occasional flashes; but seems to come out more decidedly at rather higher pressures, at least in hydrogen.

The series of bands near L, well-developed in the flame, but not seen at all in the arc or spark, look very much like the spectrum of a compound, but we have not been able to trace them to any particular combination. Sparks in air, nitrogen, and hydrogen have alike failed to produce them. The very strong, rather diffuse triplet at M, with which they end, so closely resembles in general character the other magnesium triplets, that it may well be connected with that constitution of the magnesian particle which gives rise to the triple sets of vibrations in other cases, but, if so, its presence in the flame alone is not easily explained.

The occurrence of this triplet in the ultra-violet, and of the remarkable series of bands associated with it, as well as the extraordinary intensity of the still more refrangible line at wave-length 2850, which is strongly reversed in the spectrum of the flame, corroborates what the discovery of the ultra-violet spectrum of water had revealed, that substances at the temperatures of flames while giving in the less refrangible part of the spectrum more or less continuous radiation, may still give, in the regions of shorter wave-length, highly discontinuous spectra, such as have formerly been deemed characteristic of the highest temperatures. This subject we will not discuss further at present, but simply remark what we have stated formerly, that "it opens up questions as to the enormous power for radiation of short wave-length of gaseous bodies at the comparatively low temperature of flame with regard to which we are accumulating facts."

In the arc and spark, but not in the flame, we have next a very striking group of two very strong lines at wave-lengths about 2801 and 2794, and a quintuple group of strong but sharp lines above them. The former are usually reversed in the spark with jar, and all are reversed in the arc when much magnesium is present. There are also several single lines in the visible part of the spectrum common to the arc and spark. All of these may be lines developed by the high temperature of the arc and spark. An indigo and a violet line in the arc have not been traced in the spark, but their non-appearance may be due to the same cause as that above suggested for the

non-appearance of the higher triplets, the smallness of the incandescent mass in the spark.

A pair of lines in the arc near U appear to be represented in the spark by an equally strong, or stronger, pair near but not identical in position. The possibility of such a shift, affecting these two lines only in the whole spectrum and affecting them unequally, must in the present state of our knowledge be very much a matter of speculation. Perhaps sufficient attention has not hitherto been directed to the probability of vibrations being set up directly by the electric discharge independently of the secondary action of elevation of temperature. Some of the observations above described, and many others well known, indicate a selective action by which an electric discharge lights up certain kinds of matter in its path to the exclusion of others; and it is possible that in the case of vibrations which are not those most easily assumed by the particles of magnesium, the character of the impulse may slightly affect the period of vibration. The fact that, so far as observations go, the shift in the case of this pair of magnesium lines is definite and constant, militates against the supposition suggested. On the other hand, the ghost-like pairs of lines observed in the spark below the triplet near L, suggest the idea that some of the particles have their tones flattened by some such cause.

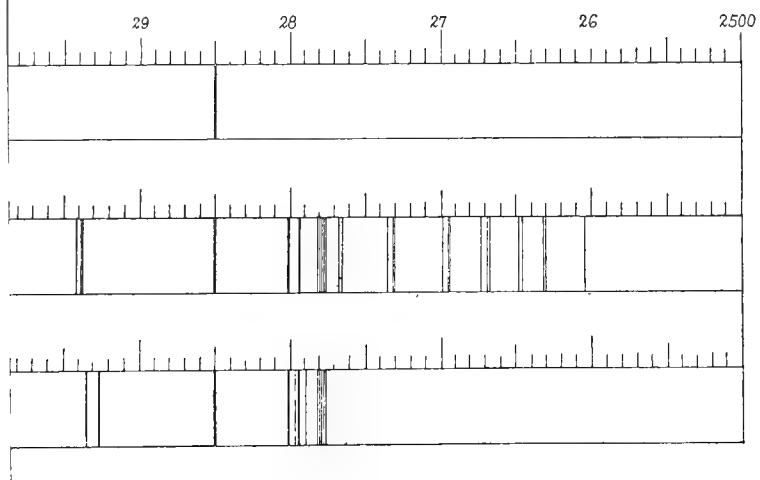
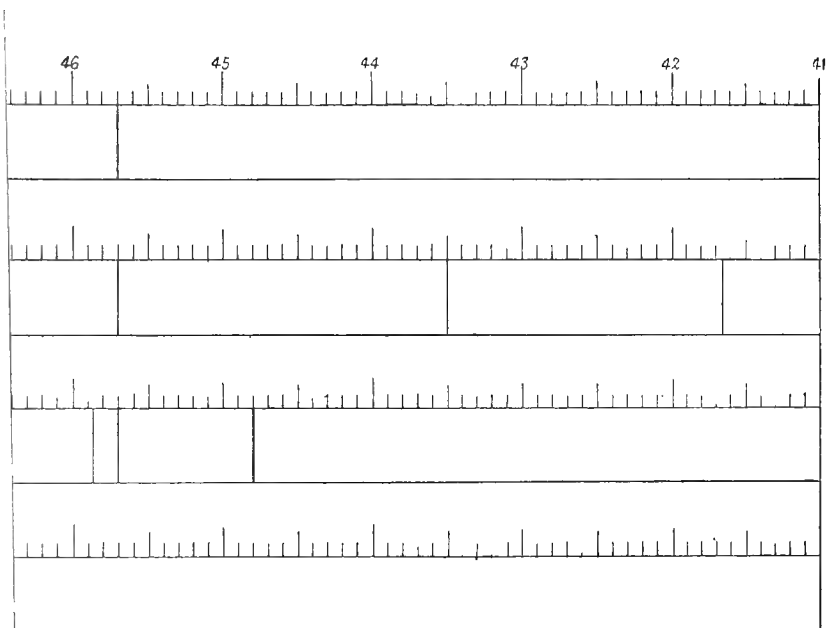
The strong pair at wave-lengths 2801, 2794 are accompanied in the spark, but not in the arc, by a much feebler, slightly more refrangible pair, but these have not the diffuse ghost-like character of those just alluded to.

These lines are phenomena of the high potential discharge in which particles are torn off the electrodes with great violence, and may well be thrown into a state of vibration which they will not assume by mere elevation of temperature.

There are two lines in the spark besides the well-known line at wave-length 4481 which have not been observed in the arc, but they are feeble and would be insignificant if it were not the fact that they, as well as the line at wave-length 4481, all short lines seen generally only about the poles, appear to be present in the solar spectrum. In the sun we seem to have all the lines common to the flame, arc, and spark (unless the line given in Ångström's map at 4570.9 be not identical as we believe it to be with the magnesium line), and possibly, judging by Rutherford's photograph, the strong triplet of the flame at M; but one line common to the arc and spark at wave-length 4703 does not appear in Ångström's map. It is hard to account for its absence, as it is present in Kirchhoff's map and in Rutherford's photograph. We have noticed, however, that when the spark is taken in hydrogen, the line at wave-length 4570 appears stronger than that at wave-length 4703, while the reverse is the case when the atmosphere is nitrogen. It is possible then that the atmosphere may, besides the resistance it offers

to the discharge, in some degree affect the vibrations of the metallic particles.

When we have made all the simplifications that we can by eliminating, as we hope we have done satisfactorily, the hydrogen-magnesium flutings, and by supposing the whole series of triplets to be harmonically related, and possibly some of the single lines also to be similarly related, we have still the fact that the chemical atoms of magnesium are either themselves capable of taking up a great variety of vibrations, or are capable by mutual action on each other, or on particles of matter of other kind, of giving rise to a great variety of vibrations of the luminiferous ether; and to trace satisfactorily the precise connexion between the occurrence of the various vibrations and the circumstances under which they occur, will require yet an extended series of observations.



ON THE IDENTITY OF SPECTRAL LINES OF DIFFERENT ELEMENTS

[*Proceedings of the Royal Society*, Vol. xxxii. (1881), pp. 225 sqq.]

THE question of the identity of spectral lines exhibited by different elements is one of great interest, because it is very improbable that any single molecule should be capable of taking up all the immense variety of vibrations indicated by the complex spectrum of iron or that of titanium, and it might therefore be expected that such substances consist of heterogeneous molecules, and that some molecules of the same kind as occur in these metals should occur in more than one of the supposed elements. Further, the supposed identity of certain lines in the spectra of more than one element has been made by Mr Lockyer the ground of an argument in support of a theory as to the dissociation of chemical elements into still simpler constituents, and in reference to this he wrote (*Proc. Roy. Soc.*, Vol. xxx, p. 31), "the 'basic' lines recorded by Thalén will require special study with a view to determine whether their existence in different spectra can be explained or not on the supposition that they represent the vibrations of forms, which, at an early stage of the planet's history, entered into combination with other forms, differing in proximate origin, to produce different 'elements.'"

Young, on examining with a spectroscope of high dispersion the 70 lines given in Ångström's map as common to two or more substances, has found that 56 are double or treble, 7 more doubtful, and only 7 appear definitely single (*American Journal of Science*, Vol. xx, 119, p. 355), and he remarks, "The complete investigation of the matter requires that the bright line spectra of the metals in question should be confronted with each other and with the solar spectrum under enormous dispersive power, in order that we may be able to determine which of the components of each double line belongs to one and which to the other element." It is this confronting of the bright line spectra of some of the terrestrial elements which we have attempted, and of which we now give an account. For the dispersion we have used a reflecting grating similar to that used by Young, with 17,296 lines to the inch, and a ruled surface of about $3\frac{1}{2}$ square inches; telescope

and collimator, each with an aperture of $1\frac{1}{2}$ inch and focal length 18 inches, the lenses being of quartz, cut perpendicularly to the axis and unachromatised, giving a very good definition with monochromatic light. The chromatic aberration is in this case an advantage, for when the telescope is in focus for lines in the spectrum of any given order, the overlapping parts of spectra of different orders are out of focus, and their brightness consequently more or less enfeebled. We have sometimes used green or blue glasses to enhance this result. The telescope and the collimator were generally fixed at about 45° , the collimator being more nearly normal to the grating than the telescope, and the grating moved to bring in successive parts of the spectra. For the parts of the spectra less refrangible than the Fraunhofer line E the spectrum of the third order was employed, for the more refrangible rays that of the fourth order. The source of light was the electric arc taken in a crucible of magnesia or lime; and for the examination of any supposed coincidence first one metal was introduced into the crucible and the line to be observed placed on the pointer of the eye-piece, the second metal was next introduced, and then in most cases, as detailed below, *two* lines were seen where only one was visible before, and the pointer indicated which of the two belonged to the metal first introduced. In some cases where both metals were already in the crucible, we had to reinforce the spectrum of one of the metals by the introduction of more of that metal, which generally brought out the spectrum of that metal more markedly than the other, and enabled us to distinguish the lines with a high degree of probability. Thus the crucibles of magnesia, or the carbons, always contain sufficient lithium to shew the orange line and the calcium line heretofore supposed coincident with it (wave-length 6101.9), but we observed these lines quite distinct and separated by a distance, estimated by the eye in comparison with the distance of neighbouring titanium lines, at about one division of Ångström's scale. On dropping a minute piece of lithium carbonate into the crucible the less refrangible line was seen to expand, and for a short time to be reversed, the other line remaining narrow and quite unaltered. When the lithium had evaporated, and both lines were again narrow, a small piece of Iceland spar was dropped into the crucible, which immediately caused the expansion, and on one occasion the reversal, of the more refrangible line, while now the less refrangible line was unaffected.

In this way we satisfied ourselves that the calcium line is the more refrangible of the two, and is probably represented by the line at wave-length 6101.9 in Ångström's normal solar spectrum, while the lithium line appears to be unrepresented.

In the case of iron, which gives such a multitude of lines, it was *à priori* probable that some lines would be coincident, or nearly so, with lines of other elements; and in fact we find that in five-sixths of the supposed

coincidences lines of iron are involved. We have, therefore, chiefly directed our attention to iron lines.

Taking iron and titanium, we find that we can resolve the lines at the wave-lengths following :—

6064·7* is a wide double, the iron line less refrangible than the titanium by something like a division on Ångström's scale. Young did not resolve this line, probably because he was looking for a much closer double line.

5714·09. A very close double, the iron the less refrangible, but not in Thalén's list.

5661·65. A double titanium line, but there appears to be a single iron line between the titanium lines.

5489·05. A titanium line, but we could not see any iron line in the arc at this place, and no such iron line is in Thalén's list.

5486·94. The iron line is more refrangible than the titanium.

5446·07. Rather a close double, the iron line the less refrangible.

5428·96. A wider double, the iron line the less refrangible.

5403·28. The iron line in this is the more refrangible.

5396·19. The iron line is the less refrangible.

5006·72. We have not resolved this line; but it is not given as an iron line in Thalén's list.

4990·48. We have not resolved this line; but it is a very strong titanium line, and the titanium may have overpowered the iron line if they are not coincident.

4690·69. The iron line is given by Thalén as slightly less refrangible than the titanium line, but we did not resolve this line (see Appendix, p. 139).

4426·9. Not given as an iron line in Thalén's list.

4307·25. The iron line is given by Thalén as slightly more refrangible than the titanium line. We have not resolved this line, the titanium line being weak.

4293·96. The iron is given by Thalén as slightly less refrangible than the titanium, but we did not resolve this line, or make out that there is any titanium line at this place.

4287·47. This is not given as an iron line in Thalén's list.

4171·77. We have repeatedly looked for this titanium line but have not seen it in the arc.

In the case of calcium it was more difficult to resolve close doubles, because the introduction of a very small quantity of a calcium compound

* The numbers by which the lines are here designated are the wave-lengths of the corresponding Fraunhofer lines taken from the catalogue of oscillation frequencies in the *Report of the British Association*, 1878, p. 37.

into the arc for the purpose of identification caused such an expansion of the calcium lines as to overpower in many cases their weaker neighbours.

6461·98. Not down as an iron line in Thalén's list. If it be an iron line, we are unable to distinguish it from the calcium line (see Appendix, p. 139).

5601·84. The iron line in this double is less refrangible than the calcium line.

5597·31. A rather close double in which the iron line is the more refrangible.

5348·75. Clearly double, the iron line less refrangible than the calcium line.

5269·59. A very close double, the iron line less refrangible than the calcium.

5041·32. A close double, but distinctly separable, the iron line the less refrangible. Kirchhoff gives the iron and calcium lines as separate, but the calcium line less refrangible than the iron.

4877·57. We could not resolve this line; though Young has resolved the corresponding solar line.

4585·36 } There are no iron lines at these places in Thalén's list, nor
4578·37 } could we detect any in the arc though the positive pole was
4580·93 } of iron.

4407·8 seems to be an iron line, though not in Thalén's list, but the calcium line, if there be one at this place in the arc, is so faint that we could not certainly make it out.

4379·16 also seems to be an iron line not in Thalén's list, but we could find no calcium line in the arc corresponding to it.

4375·46 is not given as a calcium line in Thalén's list, and we could see no calcium line at this place.

4307·25 seems to be a very close double, not distinctly divisible, as both lines are somewhat diffuse, but the iron a little less refrangible if it expands symmetrically, and so given by Kirchhoff and by Thalén.

4301·95. The iron line here is faint, and it is more refrangible than the calcium line.

4298·56. Close but distinctly divisible double, the iron less refrangible than the calcium line.

4271·33 had the appearance of a very close double, as when calcium chloride was introduced into the crucible, the line expanded more on its less refrangible side, as if the iron line were rather more refrangible than the calcium line, but we could not definitely separate the two. The two lines are not given as exactly coincident by Thalén.

The lines 4249·81, 4246·89, 4233, 4143·14, 4131·52 are doubtful calcium lines; at least, we could not detect any such lines when calcium chloride was

introduced into the arc, though the other calcium lines in the neighbourhood were well developed.

4097·55 does not seem to be an iron line, and we could detect no such line in the arc when the positive pole was of iron.

Of supposed common lines of nickel and iron :—

5168·48 is a close double, but the iron is less refrangible than the nickel line.

5145·87 we could not resolve, but it is not down as an iron line in Thalén's list.

5142·1 is double, and the iron line the less refrangible, but it was difficult to separate the two lines by reason of their diffuse character.

5136·9 is a very close double, the iron line more refrangible and weaker than the nickel line.

4854·85. We have not been able to find any iron line here in the arc.

Of supposed coincident lines of manganese and iron :—

5340·38 is a close double of manganese and iron, but still definitely divisible, the iron line being the more refrangible of the two.

5254·21 is a rather wide double, with the iron line the more refrangible.

4489·49, also plainly double, has the iron line more refrangible than the manganese line.

4414·77 is a close double, but distinctly separable, the iron line the less refrangible.

4054·48. There is a faint iron line here slightly more refrangible than the manganese line.

The magnesium and iron lines in b_4 are separable, the iron line being less refrangible.

Of chromium lines supposed coincident with iron lines :—

5207·78 is plainly double, the iron line being the less refrangible.

5203·88 not clearly resolved, but the iron line seems the less refrangible.

4654·07. We failed to detect any chromium line at this place, though the chromium line at 4646·6 was bright and strong, as well as a line at 4650·5.

4646·6 we could not resolve, but Thalén gives no line of iron in his list at this place.

4369·27 does not appear to be an iron line; we could detect no such line in the arc, and it is not given in Thalén's list. There is an iron line about one division of Ångström's scale less refrangible.

Of supposed coincident lines of iron and cobalt :—

5265·94 is decidedly double, and the more refrangible of the two lines due to cobalt.

5352·57 we did not resolve with certainty, but cobalt expanded the line more on the less refrangible side.

5681·52. The iron line here is decidedly more refrangible than that of sodium.

We have examined further the supposed coincident lines of cobalt and calcium, and of chromium and calcium, and find that 6121·34 is plainly resolvable, and the cobalt line is the less refrangible of the two.

4289·44 and 4274·63 are both close doubles, with the chromium lines the less refrangible. The latter line is difficult to resolve.

5856·6 is plainly resolvable, the calcium line more refrangible than the nickel line.

5480·29. This is a double line of titanium, and the strontium line is more refrangible than either titanium line. They form a not very close triplet.

5424·8. The barium line lies between the titanium line and the iron line next it (5423·7), and the iron line is a very little more refrangible than the barium line.

The indium line 4101·2 we found very difficult to separate from the hydrogen line (*h*), as the latter had to be taken from the spark in a tube, and is both faint and diffuse, but several observations all led to the conclusion that the indium line is very slightly less refrangible than that of hydrogen.

We have also directly compared the iron line at 5316·07 with the solar spectrum, and found that the iron line corresponds with the less refrangible of the two solar lines at this place, so that the coronal line is in all probability the other line of the pair.

There are still a few cases of supposed coincidences which we have not examined. The results which we have recorded strongly confirm Young's observations, and leave, we think, little doubt that the few as yet unresolved coincidences either will yield to a higher dispersion, or are merely accidental. It would indeed be strange, if amongst all the variety of chemical elements, and the still greater variety of vibrations which some of them are capable of taking up, there were no two which could take up vibrations of the same period. We certainly should have supposed that substances like iron and titanium, with such a large number of lines, must each consist of more than one kind of molecule, and that not single lines, but several lines of each, would be found repeated in the spectra of some other chemical elements. The fact that hardly single coincidences can be established is a strong argument that the materials of iron and titanium, even if they be not homogeneous, are still different from those of other chemical elements. The supposition that the different elements may be resolved into simpler

constituents, or into a single one, has long been a favourite speculation with chemists; but however probable this hypothesis may appear, *à priori*, it must be acknowledged that the facts derived from the most powerful method of analytical investigation yet devised give it scant support.

Appendix. May 13, 1881.

The following supposed coincidences have been resolved, in addition to those before mentioned:—

6449·27. This is rather a wide double, the calcium line being more refrangible than that of barium.

6461·98. This is a close double, but the iron is less refrangible than the calcium line.

6438·35. A wide double, the cadmium more refrangible than the calcium line.

6407·38. The iron line is decidedly more refrangible than the strontium line.

4690·69. Not resolved before because of the faintness of the iron line, which is less refrangible than the titanium line.

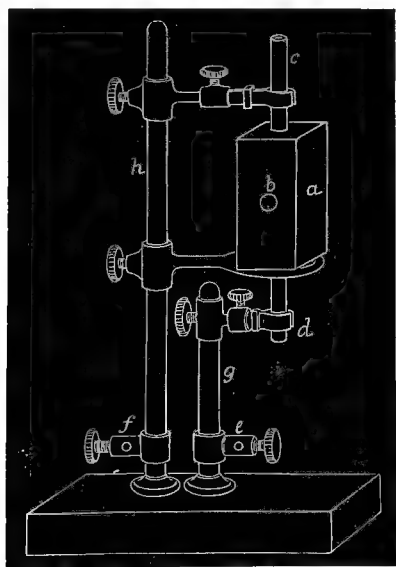


Figure representing the arrangement of crucible by which most of the observations in the foregoing paper were made. *a*, block of dense magnesia; *b*, horizontal hole for observation; *c*, upper perforated carbon through which substances were dropped into the arc; *d*, lower carbon, sometimes drilled and filled with metal; *e*, connexion for positive electrode; *f*, connexion for negative electrode; *g* and *h*, brass pillars fixed on wooden block.

ON THE REVERSAL OF THE LINES OF METALLIC VAPOURS.

No. VIII. (IRON, TITANIUM, CHROMIUM, AND ALUMINIUM)

[*Proceedings of the Royal Society*, Vol. xxxii. (1881), pp. 402 sqq.]

IN our last communication on this subject we observed (*supra*, p. 64) that iron introduced as metal, or as chloride, into the electric arc, in a lime crucible, in a way which had proved successful in the case of many other metals, gave us no reversals. We succeeded, however, in reversing some ten of the brightest lines of iron, mostly in the blue and violet, by passing an iron wire through one of the carbons, so as to keep up a constant supply of iron in the arc. Considering the great number of iron lines, and that so many of them are strongly represented amongst the Fraunhofer lines, it seemed somewhat surprising that it should be difficult to obtain a reversing layer of iron vapour in the arc inclosed as we use it in an intensely heated crucible. A like remark might be made respecting titanium, which is almost as well represented as iron in the Fraunhofer lines, but has heretofore given us no reversals. Almost the same might be said of chromium, except that the number of chromium lines is so much less than that of either of the other two metals.

We have since found that most, if not all, of the strong lines of these three metals may be reversed by proper management of the atmosphere and supply of metal in the crucible. Indeed, with regard to iron we have found that the method employed with other metals was successful so far as the ultra-violet rays were concerned, though it failed for less refrangible rays. When iron has been put into the crucible through which the arc of a Siemens dynamo-electric machine is passing, and then fragments of magnesium dropped in from time to time, most of the strong ultra-violet lines of iron are reversed. The magnesium seems to supply a highly reducing atmosphere, and to some extent carry with it the iron vapour. It also produces a good deal of continuous spectrum, at least in certain regions, and against this the iron lines are often depicted on the photographic plates sharply reversed. In this way we have observed the reversal

of the strong iron lines about the solar lines L and M, four strong lines below N, the line O, all the strong lines from S₂ to U inclusive, and two strong groups still more refrangible.

Potassium ferrocyanide introduced into the arc instead of magnesium gives a reversal of the same lines as are mentioned in the foregoing paragraph.

Iron wire fed in through a perforated pole gives reversals of the highest group (wave-length 2492 to 2480), but with the lines so much expanded as to form broad absorption-bands instead of lines.

With a vertical arrangement of the carbons, similar to that used by us for resolving the fine double lines (*supra*, p. 139), and a stout iron wire in the axis of the lower (positive) carbon, many more lines in the visible part of the spectrum are seen expanded and reversed. This effect is sometimes enhanced by leading into the crucible through the upper carbon, which is perforated for the purpose, a very gentle stream of hydrogen gas; the stream must be no more than is just sufficient to give a tiny flame at the mouth of the crucible; a stronger stream diminishes the amount of metallic vapour, probably by its cooling action, and lessens the effect. By this treatment, some of the strongest lines of iron remain reversed for some time, the weaker lines are seen to expand and be reversed for a few seconds at a time, when, from a change in the intensity of the current, or some other reason, a larger amount of metal is volatilized and shews itself by burning in brilliant scintillations at the mouth of the crucible.

A list of the iron lines reversed, designated by their approximate wave-lengths, is subjoined.

5614·5
 5585·5
 5445·6
 5428·5
 5405
 5396
 5370·5
 5327 the more refrangible of this pair.
 5268·5 E
 5226 the less refrangible of this double line.
 5166·8 b₄
 5064
 5072
 4956·5 both lines of pair, the less refrangible strongly.

	4919·7	3727 M	3007·5	2744·7
	4918	3722	3006·5	2743
	4890·5	3720	3000	2741·3
	4890	3707·5	2999	2736·2
4871 both lines of pair.	3705·5	2994 <i>t</i>	2722·7	
	4414·5	3647	2984	2720
	4404	3631	2982	2718
	4382·5	3502	2974	2549·5
	4325	3492	2971	2545·5
	4314·5	3475	2967·5	2541
	4307 G	3465·5	2965·5	2535·7
4271 both lines of pair.	3440 O	2957	2534	
	4071	3402·5	2953·5	2529
	4063	3272*	2948 U	2528·6
	4045	3246*	2941	2527·3
	3898	3099·5 S ₂	2937	2524·2
	3886	3082	2932	2523
	3859	3072	2929	2518·3
	3856	3057	2912	2511
	3833·5	3056	2871	2502
	3827·5	3046·5 <i>s</i>	2866·3	2492
	3825	3041	2860·8	2491·6
	3824	3036·5	2836·4	2491
	3820 L	3030	2829·8	2489·3
	3815	3024·5	2824·2	2485·4
	3767	3022·5	2767·3	2484·6
	3763·5	3020 T	2755·2	2481
	3757·5	3017·5	2754·3	2480
	3745·5	3016·5	2749	2474
	3736·5	3008·5	2748	2465
	3734·5			

It is by no means always the strongest lines which are reversed. For instance, in the group of lines between wave-lengths 5428·5 and 5396 there are four strong lines 5423·5, 5414·6, 5403, and 5382·4, which are all much expanded and diffuse when iron is introduced into the arc, but have not been seen reversed by us, while three other lines—5396, 5405, and 5428·5—are well reversed, but not much expanded. Considering the enormous complexity of the iron spectrum, which probably reaches to something like a thousand distinct vibrations, we should expect to find a greater variation in the relative strength and reversibility of the lines of this metal, according to the circumstances in which it is placed, than we find in the

* It is possible that these may have been the copper lines which were reversed, and not the iron lines, which are nearly identical in position.

case of metals giving simpler spectra. So that we may say, on the whole, that the phenomena in the case of iron are of much the same general character as we have observed before in the case of other metals; but the number of observations to be made on so extensive a subject renders it extremely difficult to come to any general conclusions.

When the perforation of the lower carbon is filled with titanium cyanide instead of the iron wire, the titanium lines come out very brilliantly and steadily, and many of them, especially in the green and blue parts of the spectrum, are expanded and reversed. We give a list of those we have observed to be reversed.

6260	5038	4535·5	4617
6257 both lines of pair.	5036	4535	4305
5223	5035	4533·2	4299·5
5209	5013	4531·7	4299
5192	5007	4690·5	4298
5129	4999	4681	4295
5064	4990	4666·5	4290·7
5039	4981	4655·5	

In the case of chromium, introduced into the crucible either as oxide or as bichromate of ammonia, there were no reversals until a gentle current of hydrogen or of coal gas was led in through the perforated carbon. This brought out the triplet in the green, wave-lengths 5207, 5205, 5203, sharply and steadily reversed, and likewise the three strong lines in the indigo, wave-lengths 4289, 4274, 4253; also a triplet near N at wave-lengths about 3578, 3593, 3606, apparently coincident with strong lines in Cornu's map of that part of the solar spectrum, and a rather strong double line just below O at about wave-length 3446. The reversal of another chromium line at about wave-length 3217 is doubtful. A triplet, at wave-lengths 2799·8, 2797, 2794, is more easily reversed than any other of the chromium lines. This triplet is generally strongly developed whenever a compound of chromium is introduced into the crucible, so that we conclude that it is due to that metal, but it is sometimes visible in the photographs when other chromium lines are not seen. A still more refrangible chromium line, wave-length about 2779·6, is also frequently reversed by a gentle current of hydrogen.

The two aluminium lines near S are frequently reversed when a fragment of the metal is dropped into the crucible, the less refrangible line, wave-length 3091·5, being more strongly reversed, and continuing reversed for a longer time than that at wave-length 3080·5.

ON THE ORIGIN AND IDENTITY OF SPECTRA

[*Proceedings of the Royal Institution*, Vol. ix. (1881), pp. 674 sqq.]

Origin and Identity of Spectra.

ON a former occasion I detailed the results of a joint research made in consort with my esteemed friend Professor Liveing, on the "Reversibility of the Rays of Metallic Vapours*." The present lecture will be devoted to a record of the results of our work in relation to three disputed questions in spectroscopic investigation, viz. (1) the Carbon Spectrum, (2) the Magnesium Spectrum, and (3) the Identity of the Spectral Lines of different Elements.

Spectrum of Carbon Compounds.

The spectrum of the flame of hydrocarbons burning in air has been repeatedly described, first by Swan in 1856, and afterwards by Attfield, Watts, Morren, Plücker, Huggins, Boisbaudran, Piazzzi Smyth, and others. The characteristic part of this spectrum consists of four groups of bands of fine lines in the orange, yellow, green, and blue respectively, which are hereafter referred to as the hydrocarbon bands. These four groups, according to Plücker and Hittorf, also constitute the spectrum of the discharge of an induction-coil in an atmosphere of hydrogen between carbon electrodes. They are also conspicuous in the electric discharge in olefiant gas at the atmospheric and at reduced pressures.

Plücker and Hittorf notice the entire absence in the flame of olefiant gas of the two bright groups of lines (blue and violet as described below) characteristic of the flame of cyanogen.

Several observers have described the spectrum of the flame of burning cyanogen. Faraday, as long ago as 1829, called the attention of Herschel and Fox Talbot to it, and the latter, writing of his observations†, points out as a peculiarity that the violet end of the spectrum is divided into three portions with broad dark intervals, and that one of the bright

* *Proceedings of the Royal Institution*, Vol. ix, p. 204.

† *Phil. Mag.*, Ser. iii, Vol. iv, p. 114.

portions is ultra-violet. More recently Dibbits, Morren, Plücker and Hittorf have particularly described this spectrum. Dibbits* mentions in the cyanogen flame fed with oxygen a series of orange and red bands shaded on the less refrangible side (*i.e.* in the opposite way to the hydrocarbon bands), the four hydrocarbon bands more or less developed, a group of seven blue lines, a group of two or three faint blue (indigo) lines, then a group of six violet lines, and, lastly, a group of four ultra-violet lines. When the cyanogen is burnt in air, the hydrocarbon bands are less developed, and the three faint indigo lines are scarcely visible, but the rest of the spectrum is the same, only less brilliant.

Plücker and Hittorf† state that in the flame of cyanogen burning in air under favourable circumstances, the orange and yellow groups of lines characteristic of burning hydrocarbons are not seen, the brightest line of the green group appears faintly, the blue group is scarcely indicated; but a group of seven fluted bands in the blue, three in the indigo, and seven more in the violet, are well developed, especially the last. When the flame was fed with oxygen instead of air, they state that an ultra-violet group of three fluted bands appeared. They notice also certain red bands with shading in the reverse direction, which are better seen when the flame is fed with air than with oxygen. Other observers give similar accounts, noticing the brilliance of the two series of bands in the blue and violet above-mentioned, and that they are seen equally well in the electric discharge through cyanogen.

Ångström and Thalén, in a memoir "On the Spectra of Metalloids‡," contend that the channelled spectra of the hydrocarbon and cyanogen flames are the spectra respectively of acetylene and cyanogen, and not of carbon itself, and that in the flame of burning cyanogen we sometimes see the spectrum of the hydrocarbon superposed on that of the cyanogen, the latter being the brighter; and that in vacuum tubes containing hydrocarbons the cyanogen spectrum observed is due to traces of nitrogen.

No chemist who remembers the extreme sensibility of spectroscopic tests, and the difficulty, reaching almost to impossibility, of removing the last traces of air and moisture from gases, will feel any surprise at the presence of small quantities of either hydrogen or nitrogen in any of the gases experimented on.

Mr Lockyer§ obtained a photograph of the spectrum of the electric arc in an atmosphere of chlorine, which shews the series of fluted bands in the ultra-violet, on the strength of which he throws over the conclusion of Ångström and Thalén, and draws inferences regarding the existence of carbon vapour above the chromosphere in the coronal atmosphere of

* *Pogg. Ann.*, 1864, Vol. cxxii, p. 512.

† *Phil. Trans.*, 1865, pp. 16 sqq.

‡ *Nova Acta, Roy. Soc. Upsala*, Vol. ix.

§ *Proc. Roy. Soc.*, Vol. xxvii, p. 308.

the sun, which, if true, would be contrary to all we know of the properties of carbon.

The conclusions of Ångström and Thalén have been much strengthened by the results of a series of observations carried out by Professor Liveing and myself.

Electric Arc in different Gases.

The experiments were made with a De Meritens magneto-electric machine, arranged for high tension, giving an alternating current capable of producing an arc between carbon poles in air of from 8 to 10 millims. in length. The carbon poles used were 3 millims. in diameter, and had been previously purified by prolonged heating in a current of chlorine. This treatment, though it removes a large part of the metallic impurities present in the commercial carbons, will not remove the whole, so that lines of calcium, iron, magnesium, and sodium may still be recognised in the arc. Besides the traces of metallic impurities, a notable quantity of hydrogen always remains unremovable by this treatment with chlorine.

The arc was taken in different gases inside a small glass globe (*aa* in the figure on p. 88, *supra*) about 60 millims. in diameter, blown in the middle of a tube. The two ends of the tube (*bb*) were closed with dry corks, through which were passed (1) the carbons (*cc*), inserted through two pieces of narrow glass tubing; (2) two other glass tubes (*dd*) through which currents of the different gases experimented on were passed.

The arc in the globe filled with air gave a tolerably bright continuous spectrum, on which the green and blue hydrocarbon bands were seen, also the seven bands in the indigo (wave-lengths 4600 to 4502, Watts) as in the flame of cyanogen, and much more brightly the six bands in the violet (wave-lengths 4220 to 4158, Watts) and five ultra-violet. Besides these bands, lines of iron, calcium, and sodium were visible. The arc in this case was practically taken in a mixture of nitrogen and carbonic oxide, for in a short time the oxygen of the air is converted into carbonic oxide.

On passing through the globe a current of carbonic acid gas, the bands in the indigo, violet, and ultra-violet gradually died out until they ceased to be visible continuously, and when momentarily seen were only just discernible. On the other hand, the hydrocarbon bands, yellow, green, and blue, came out strong, and were even brilliant. Lines of iron and calcium were still visible. On stopping the current of carbonic acid gas and allowing air to diffuse into the globe, the violet and ultra-violet bands soon began to appear, and presently became permanent and bright, the hydrocarbon bands remaining bright.

When a continuous current of dry hydrogen was passed through the globe, the arc, contrary to what would be expected from the behaviour of

the spark discharge in hydrogen, would not pass through more than a very short space, very much less than in air or carbonic acid gas. There was a tolerably bright continuous spectrum, with no trace of bands in the indigo, violet, or ultra-violet, and no metallic lines, with the exception of a fairly bright line in the red, which we identified, by comparison with the spark in a vacuum tube, with the C line of hydrogen. The F line, identified in like manner, was also seen as a faint diffuse band. This last line was in general overpowered by the continuous spectrum, but was regularly seen when, from some variation in the discharge, the continuous spectrum became less brilliant. This was the first occasion on which we had seen the hydrogen lines in the arc, though Secchi* states that he had seen them by the use of moist carbon poles. The hydrocarbon bands in the green and blue were at intervals well seen. Those in the yellow and orange were, owing doubtless to the smaller dispersion of the light in that region, overpowered by the continuous spectrum. Whereas when air and carbonic acid gas were used, the inside of the globe was quickly covered with dust from the disintegrated poles, scarcely any dust was thrown off when the arc was passed in hydrogen.

In nitrogen a longer arc could be formed, and the indigo, violet, and ultra-violet bands of cyanogen all came out at intervals brilliantly. The green and blue hydrocarbon bands were also well developed.

On filling the globe with chlorine, keeping a current of that gas passing through it, the arc would not pass through a greater distance than about 2 millims. No metallic lines were visible. At first the violet bands, as well as the green and blue hydrocarbon bands, were visible; but gradually, when the current of chlorine had been passing for some minutes, there was nothing to be seen but a continuous spectrum with the green and blue hydrocarbon bands. Neither of these bands were strong, and at intervals the blue bands disappeared altogether.

The arc would not pass in a current of carbonic oxide through any greater space than in chlorine. There was much continuous spectrum; the yellow, green, and blue hydrocarbon bands were well seen, some of the indigo bands were just discernible, the violet had nearly, and the ultra-violet quite, gone from sight. No trace of the carbonic oxide bands, as seen in the spark discharge in that gas, was visible. This is the more remarkable since under similar circumstances two of the characteristic lines of hydrogen were seen.

In nitric oxide a very long arc could be obtained. The violet and ultra-violet cyanogen bands were well seen, the indigo bands were seen, but weaker. The blue and green hydrocarbon bands were also seen well when

* *Compt. Rend.* (1873), Vol. lxxvii, p. 177.

the arc was short, not so well when the arc was long. Many metallic lines of iron, calcium, and magnesium were seen.

In ammonia only a short arc could be obtained. All the bands were faint, but the indigo and violet and ultra-violet cyanogen bands were always visible.

These experiments with different gases eliminate to a large extent the influence of electric conductivity on the character of the spectrum.

Apart from the relative electric conductivity of gases, it is clear, from the experiments, that the length and character of alternating electric discharges between carbon poles in different gases does not follow the law which we should expect. It will require a prolonged series of experiments to arrive at definite conclusions on this matter; but, in the meantime, it is highly probable that one of the main factors in producing these remarkable variations in the arc will be found to be the relative facility with which the carbon of the poles combines with the gaseous medium.

On a review of the above series of observations, certain points stand out plainly. In the first place, the indigo, violet, and ultra-violet bands, characteristic of the flame of cyanogen, are conspicuous in the arc taken in an atmosphere of nitrogen, air, nitric oxide, or ammonia, and they disappear almost, if not quite, when the arc is taken in a non-nitrogenous atmosphere of hydrogen, carbonic oxide, carbonic acid, or chlorine. These same bands are seen brightly in the flames of cyanogen and hydrocyanic acid, but are not seen in those of hydrocarbons, carbonic oxide, or carbon disulphide. The conclusion seems irresistible that they belong to cyanogen; and this conclusion does not seem to us at all invalidated by the fact that they are seen weakly, or by flashes, in the arc or spark taken in gases supposed free from nitrogen, on account of the extreme difficulty of removing the last traces of air. They are never, in such a case, the principal or prominent part of the spectrum, and in a continuous experiment they are seen to fade out in proportion as the nitrogen is removed. This conclusion is strengthened by the recent discovery that cyanogen is always generated in the electric arc in atmospheric air.

The green and blue bands, characteristic of hydrocarbon flames, are well seen when the arc is taken in hydrogen; but, though less strong when the arc is taken in nitrogen or in chlorine, they seem to be always present in the arc, whatever the atmosphere. This is what we should expect, if they be due, as Ångström and Thalén suppose, to acetylene; for we have found that the carbon electrodes always contain, even when they have been long treated with chlorine at a white heat, a notable quantity of hydrogen.

The hydrocarbon bands are well developed in the blowpipe flame, that is under conditions which appear, at first sight, unfavourable to the existence

of acetylene. We have, however, satisfied ourselves, by the use of Deville's aspirator, that acetylene may be withdrawn from the interior of such a flame, and from that part of it which shews the hydrocarbon bands brightly.

The question as to whether these bands are due to carbon itself or to a compound of carbon with hydrogen, has been somewhat simplified by the observations of Watts and others on the spectrum of carbonic oxide. There is, we suppose, no doubt now that that compound has its own spectrum quite distinct from the hydrocarbon flame spectrum. The mere presence of the latter spectrum feebly developed in the electric discharge in compounds of carbon supposed to contain no hydrogen, appears to us to weigh very little against the series of observations which connect this spectrum directly with hydrocarbons.

In the next place, it appears, from experiments, that the development of the violet bands of cyanogen, or the less refrangible hydrocarbon bands, is not a matter of temperature only. For the appearance of the hydrogen lines C and F in the arc taken in hydrogen, indicates a temperature far higher than that of any flame. Yet the violet bands disappear at that temperature, and the green bands are well developed. The violet bands are, nevertheless, seen equally well at the different temperatures of the flame, arc, and spark, provided cyanogen be the compound under observation in the flame, and nitrogen and carbon are present together at the higher temperatures of the arc and spark.

The question of the constitution of comets, since the discovery by Huggins* that the spectra of various comets are identical with the hydrocarbon spectrum, naturally leads to some speculation in connection with the conclusions to which our experiments point. Provided we admit that the materials of the comet contain ready-formed hydrocarbons and that chemical or electrical actions may take place, generating a high temperature, then the acetylene spectrum might be produced at temperatures no higher than that of ordinary flames without any trace of the cyanogen spectrum, or of metallic lines. Such actions might be brought about by the tidal disturbances involving collisions and projections of the constituents of the swarms of small masses circulating in orbits round the sun, which we have every reason to believe constitute the cometic structure. If, on the other hand, we assume only the presence of uncombined carbon and hydrogen, we know that the acetylene spectrum can only be produced at a very high temperature; and if nitrogen were also present, that we should at such a temperature have the cyanogen spectrum as well. Either then the first supposition is the true one, not disproving the presence of nitrogen; or else the atmosphere which the comet meets is hydrogen only and contains no nitrogen.

* *Proc. Roy. Soc.*, Vol. xvi, p. 386; Vol. xxiii, p. 154; *Phil. Trans.*, 1868, p. 556.

The Flame of Cyanogen.

The diagram on page 102 (*supra*, Fig. 1) shews the relative position of the bands in that part of the spectrum of the flame of cyanogen fed with a jet of oxygen which is more refrangible than the Fraunhofer line F. Only those bands which are less refrangible than the solar line L have been before described, but photographs shew another set of two shaded bands slightly less refrangible than the solar line N accompanied by a very broad diffuse band of less intensity on the more refrangible side of N; also a strong shaded band, which appears to be absolutely coincident with the remarkable shaded band in the solar spectrum, which has been designated by the letter P: and near this, on the less refrangible side, a much fainter diffuse band, which also seems to coincide with a part of the solar spectrum sensibly less luminous than the parts on either side of it. Watts found that the spectrum of the cyanogen flame did not disappear when the flame was cooled by diluting the cyanogen with carbonic acid; and we have found that it retains its characters when the cyanogen is burnt in nitric oxide. The flame in the last case must be one of the hottest known, from the large amount of heat evolved in the decomposition of cyanogen and nitric oxide, namely, 41,000 and 43,300 units respectively. There is in the case of cyanogen, as in the case of so many other substances, a difference in the relative intensities of the different parts of the spectrum at different temperatures, but no other change of character.

On the theory that these groups of lines are the product of an exceptional temperature in the case of the cyanogen flame, it is inconceivable that they could disappear by combustion in oxygen, instead of in ordinary air. Our observations accord with the statement of Morren, Plücker, Hittorf, and Thalén, that a cyanogen flame, fed with oxygen, when it is intensely luminous, still yields these peculiar groups. We have found these peculiar groupings in the flame when it had a current of oxygen in the middle, and was likewise surrounded outside with oxygen. There is nothing remarkable in the fact that only a continuous spectrum is seen to proceed from any hydrocarbon or nitrocarbon burning in excess of oxygen, as we know from Frankland's experiments that carbonic acid and water vapour, at the high temperature of flame under compression, give in the visible portion a continuous spectrum. In fact, this is what we should anticipate, provided intermediate, and not the final, compounds are the active sources of the banded spectrum.

Each of the five sets of bands shewn in the diagram is attended on its more refrangible side by a series of rhythmical lines extending to a considerable distance, not shewn in the diagram, but easily seen in the photographs.

Coal gas burning in oxygen gives no bands above that near G within the range of the diagram; but beyond this our photographs shew a spectrum of a character quite different from that at the less refrangible end. The most remarkable part of this spectrum is a long series of closely set strong lines, filling the region between the solar lines R and S, and ending abruptly with two strong lines a little beyond S. These are lines of various intensities, not regularly arranged so as to give shaded bands like those in the less refrangible part of the spectrum. Beyond these lines there is another large group of lines, not so strong or so closely set, but sharp and well defined. This peculiar part of the spectrum is really due to the vapour of water, and shall be discussed in the sequel.

Spark Discharge in various Gases.

Mr Lockyer's experiments on the spectrum of carbon compounds are directly opposed to the results given above, as will be understood by the following extract from one of his papers on the subject*:—"I beg permission, therefore, in the meantime, to submit to the notice of the Society an experiment with a tube containing CCl_4 †, which, I think, establishes the conclusions arrived at by prior investigators. And I may add that it is the more important to settle the question, as Messrs Liveing and Dewar have already based upon their conclusions theoretical views of a kind which appear to me calculated to mislead, and which I consider to have long been shewn to be erroneous." The following experiments have been made to test the accuracy of our previous work, and to confirm or disprove Mr Lockyer's views.

The form of sparking tube employed was similar to that used by Salet. This was attached by thick rubber tubing to a straight glass tube of which one half, about 6 inches long, was filled with phosphoric anhydride, and the other half with small fragments of soda-lime to prevent any chlorine, from the decomposition of the tetrachloride by the spark, from reaching the Sprengel pump. The tetrachloride used had been prepared in our own laboratory, and fractionated until it had a constant boiling point of 77°C . Sufficient of it was introduced into the sparking tube to fill nearly one quarter of the bulb at the end, and the whole interior of the tube thoroughly wetted with it in order to facilitate the removal of the last traces of air.

When the tube containing the tetrachloride had been so far exhausted that little but condensable vapours were pumped out, the bulb was heated so as to fill the apparatus with vapour of tetrachloride, the pump still going, and this was repeated as long as any incondensable gas was extracted. Sparks were then passed through the tube for a short time, the

* *Proc. Roy. Soc.*, Vol. xxx, p. 336.

† Carbon tetrachloride.

pump still being kept going. After a short time it was unnecessary to keep the pump going, as all the chlorine produced by decomposition of the tetrachloride was absorbed by the soda-lime. On now examining the spectrum, no trace of any of the bands we ascribe to nitrocarbons could be detected, either by the eye or by photography, however the spark might be varied. The violet lines of chlorine described by Salet were more or less visible, coming out brightly when a condenser was used. Several tubes were treated in this way, and many photographs taken, but always with the same result; no trace appeared of either the seven blue, the six violet, the five ultra-violet, or of the still more refrangible bands of the cyanogen flame. All the photographs shewed three lines in the ultra-violet, but these do not at all resemble the nitrocarbon bands, as they are not shaded. The least refrangible of the three is nearly coincident with the middle maximum in the ultra-violet set of five bands, but the other two do not coincide with any of these maxima. When a condenser is used, these three lines come out with much greater intensity, and two other triplets appear on the more refrangible side, as well as other lines. In order to compare the positions of these lines with the cyanogen bands, we have taken several photographs of the spark in tetrachloride simultaneously with a cyanogen flame, the latter being thrown in by reflection in the usual way.

Not one of many photographs so taken shewed any traces of the cyanogen bands. The general character of the violet part of the spectrum of the spark in carbon tetrachloride taken without a condenser (but not the exact position to scale of wave-lengths of all the lines) is shewn in Fig. 2 of the diagram on p. 102. In Fig. 3 of the same diagram are shewn the brightest of the additional lines which come out with the use of a condenser. Photographs of sparks taken in hydrochloric acid shewed a precisely similar group of ultra-violet lines, so that the three lines which our photographs shew amongst the five ultra-violet nitrocarbon bands are due to chlorine.

Having satisfied ourselves by repeated trials that pure carbon tetrachloride or trichloride, if free from nitrogen, does not give any of the bands we ascribe to nitrocarbon compounds, our next step was to determine whether the addition of nitrogen would bring them out, and if so, what quantity of nitrogen would make them visible.

For this purpose we introduced a minute fragment of bichromate of ammonia, carefully weighed, and wrapped in platinum foil, into the neck of one of the sparking tubes containing carbon tetrachloride, connected the tube to the Sprengel pump, and removed the air as before. The spark examined in the tube shewed no trace of any nitrocarbon band. A pinch-cock was now put on the rubber tube, and the bichromate heated by a spirit-lamp to decomposition (whereby it is resolved into nitrogen, water and oxide of chromium). On now passing the spark the six violet bands

were well seen. There was no change in the condition of the coil or rheotome, so that the spark was of the same character as it had been before when no nitrocarbon bands were visible, and the change in the spectrum cannot be attributed to any change in the spark. The weight of the bichromate was between '0005 and '0006 grm.; and the nitrogen this would evolve would fill just about $\frac{1}{20}$ of a cubic centimeter at atmospheric pressure. The tube held 30 cub. centims., so that vapour of carbon tetrachloride, when mixed with $\frac{1}{600}$ part of its volume of nitrogen, gives under the action of the electric spark the nitrocarbon bands distinctly. Other similar experiments confirmed this result. It is worthy of remark that the nitrocarbon bands were not seen instantaneously on the admission of nitrogen into the tube, but were gradually developed, as if it was necessary that a certain quantity of nitrocarbon compound should be formed under the influence of the electric discharge and accumulated before its spectrum became visible.

A tube, containing naphthalene, previously well washed with dilute sulphuric acid, dried and resublimed, was attached to the Sprengel pump, and treated as the tubes with tetrachloride had been. The spark in this tube likewise shewed no nitrocarbon bands. After a time the tube cracked, and then the nitrocarbon bands made their appearance, and on setting the pump going a good deal of gas was pumped out. When the air had again been pretty completely exhausted, the nitrocarbon bands were no longer visible, but gradually appeared again as air leaked through the crack. Another tube, containing a mixture of naphthalene and benzene, shewed no trace of the nitrocarbon bands.

The observation of the nitrocarbon bands in the spectrum of the spark in naphthalene was one of the reasons which led Watts at one time to ascribe these bands to free carbon.

In our first experiments with carbonic oxide the gas was made by the action of sulphuric acid on dried formate of sodium. At first the six violet cyanogen bands were well seen, and the seven blue bands faintly; but gradually, as the air became more completely expelled, the blue bands disappeared entirely, and then the violet bands so far died out that it was only by manipulating the coil that they could be made visible, and then only very faintly. A bubble of air about $\frac{1}{40}$ part of the volume of gas in the generating flask and tube, was now introduced, when almost immediately the bands reappeared brightly. As the stream of gas continued, they again gradually died away until they were represented only by a faint haze. It was subsequently found that each introduction of fresh acid into the flask was attended with a marked increase in the brightness of the nitrocarbon bands, which died away again when the current of gas was continued without fresh introduction of acid. On testing the acid it was found to contain, as is

frequently the case with sulphuric acid, a very small quantity of the oxides of nitrogen.

The difficulty of getting all the air expelled from the apparatus and reagents led us to adopt another method of making carbonic oxide. Carbonic oxide was generated by heating in a tube of hard glass in a combustion furnace a mixture of pure dry potassium oxalate with one quarter of its weight of quicklime, the mixture having been previously heated for some time to expel traces of ammonia. No trace whatever of the nitrocarbon bands could be detected in this carbonic oxide, however the spark might be varied. The pressure of the gas was reduced to 1 inch of mercury, while the spectrum was observed from time to time. Still no trace of the nitrocarbon bands could be detected. More of the oxalate was heated, and the observations repeated again and again, always with the same result. Carbonic oxide, therefore, if quite free from nitrogen, does not give, at the atmospheric or any less pressure, the nitrocarbon spectrum.

On passing the spark between carbon poles in nitrogen, the nitrocarbon bands are plainly seen; and remain visible through great variations in the character of the spark. Photographs taken, with and without the use of the condenser, shewed the violet and ultra-violet nitrocarbon bands, including those near N and P. If the nitrogen were swept out by a current of carbonic acid gas, on passing the spark the nitrocarbon bands could no longer be detected, and photographs shewed no trace of any of the ultra-violet bands.

In all the foregoing experiments the bands which Ångström and Thalén ascribe to hydrocarbons were always more or less plainly seen. Much more care than has generally been thought necessary is needed if the last traces of hydrogen and its compounds are to be removed from spectral tubes. Indeed, water cannot be completely removed from apparatus and reagents which do not admit of being heated to redness.

Thus a mixture of carbonate of sodium and boric anhydride, previously to admixture heated red hot, was introduced into one end of a piece of combustion tube, near the other end of which wires had been sealed, and the open end drawn out; the mixture was then heated, and when it was judged that all the air was expelled, the tube was sealed off at atmospheric pressure. On passing sparks through it carbonic oxide bands and oxygen lines could be seen, but no hydrogen, hydrocarbon, or nitrocarbon bands could be detected. It appears, therefore, that the application of a red heat is likely to prove a more effectual means of getting rid of moisture than the use of any desiccating agent.

Are the groups of shaded bands seen in the more refrangible part of the spectrum of a cyanogen flame, of which the three which can be detected by the eye are defined by their wave-lengths (4600 to 4502, 4220 to 4158, and

3883 to 3850), due to the vapour of uncombined carbon, or, as we conclude, to a compound of carbon with nitrogen?

The evidence that carbon can take the state of vapour at the temperature of the electric arc is at present very imperfect. Carbon shews at such temperatures only incipient fusion, and that uncombined carbon should be vaporised at the far lower temperature of the flame of cyanogen is so incredible an hypothesis, that it ought not to be accepted if the phenomena admit of any other probable explanation. On the other hand, cyanogen or hydrocyanic acid is generated in large quantity in the electric arc taken in nitrogen, and Berthelot has shewn that hydrocyanic acid is produced by the spark discharge in a mixture of acetylene and nitrogen, so that in the cases in which these bands shine out with the greatest brilliance, namely, the arc in nitrogen and the cyanogen flame, we know that nitro-carbon compounds are present. Further, we have shewn that these bands fade and disappear in proportion as nitrogen is removed from the arc. Ångström and Thalén had previously shewn the same thing with regard to the discharge between carbon electrodes; and the conclusion to which they and we have come would probably have commanded universal assent if it had not been for the fact that these bands had been seen in circumstances where nitrogen was supposed to be absent, but where, in reality, the difficulty of completely eliminating nitrogen, and the extreme sensibility of the spectroscopic test, had been inadequately apprehended.

Our argument is an induction from a very long series of observations which lead to one conclusion, and hardly admit of any other explanation. Mr Lockyer*, however, attempts to explain the disappearance of the bands when nitrogen is absent by the statement "that the tension of the current used now brings one set of flutings into prominence, and now another." This is no new observation. It is well known that variations in the discharge produce variations in the relative intensities of different parts of a spectrum. Certain lines of magnesium, cadmium, zinc, and other metals, very brilliant in the spark, are not seen, or are barely seen, at all in the arc. His remark might be applied to the spectra of compounds as well as to those of elements. Variation in the discharge accounts very well for some of the variations of intensity in the bands if they be due to a nitro-carbon; it will not, however, account for the fact observed by us, that the bands, or those of them which have the greatest emissive power, and are best developed by the particular current used, come out on the addition of a minute quantity of nitrogen, when there is every reason to think that no variation of the current occurs.

Much the same may be said with regard to the changes of the spectrum produced by changes of temperature. We cannot infer from any of these changes that the spectrum is not due to a compound.

* *Loc. cit.* p. 342.

Again, Mr Lockyer* attempts to get over the difficulties of his case by the supposition that "the sets of carbon flutings represent different molecular groupings of carbon, in addition to that or those which give us the line spectrum."

Now, until independent evidence can be adduced that carbon can exist in the state of uncombined vapour at the temperature of a cyanogen flame, and that different groupings in such vapour exist, the hypothesis here enunciated is a gratuitous one, so long as the existence of nitrocarbon compounds in the flame, arc, and spark will sufficiently explain the facts.

The observation above recorded, that there is in the spectrum of cyanogen a strong shaded band coincident with the very characteristic dark shaded band P of the solar spectrum, strengthens materially the evidence in favour of the existence of these bands in the solar spectrum; the more so, as the series of lines at P has far more of the distinctive character of the cyanogen spectrum than any other series in the ultra-violet part of the solar spectrum.

The hypothesis that if present they are due to vapour of carbon uncombined in the upper cooler region of the chromosphere seems absurd. One object of our investigations has been to determine the permanence of compounds of the non-metallic elements, and the sensitiveness of the spectroscopic test in regard to them. It appeared probable that if such compounds exist in the solar atmosphere their presence would be most distinctly revealed in the more refrangible part of the spectrum. In the meantime it is sufficiently clear that the presence of nitrogen in the solar atmosphere may be recognised through cyanogen when free nitrogen might escape detection.

The series of experiments, unless proved to be wrong, are almost conclusive proof that Mr Lockyer's views regarding the origin and variation of the carbon spectrum have no real experimental basis.

Spectrum of Magnesium.

The absorption spectrum of magnesium and of magnesium with potassium and sodium, as seen in iron tubes in a hydrogen atmosphere, described in the former lecture†, correspond to no known emission lines of magnesium. We could only ascribe their origin to the mixtures employed as distinct from the separate elements, and therefore were led to investigate the conditions under which corresponding emission lines could be produced.

In *Proc. Roy. Soc.*, Vol. xxvii (*supra*, p. 16), the emission spectrum of sparks from an induction-coil taken between magnesium points in an atmosphere of hydrogen is described as follows:—

* *Loc. cit.* p. 341.

† *Supra*, pp. 53 sqq.

"A bright line regularly appeared with a wave-length about 5210.... This line does not usually extend across the whole interval between the electrodes, and is sometimes seen only at the negative electrode. Its presence seems to depend on the temperature, as it is not seen continuously when a large Leyden jar is employed, until the pressure of the hydrogen, and its resistance, is very much reduced. When well-dried nitrogen or carbonic oxide is substituted for hydrogen, this line disappears entirely; but if any hydrogen or traces of moisture be present, it comes out when the pressure is much reduced. In such cases the hydrogen lines C and F are always visible as well. Sometimes several fine lines appear on the more refrangible side of this line between it and the *b* group, which give it the appearance of being a narrow band shaded on that side."... "In addition to the above-mentioned line, we observed that there is also produced a series of fine lines, commencing close to the most refrangible line of the *b* group, and extending, with gradually diminishing intensity, towards the blue... from forty-five to fifty being visible, and placed at nearly equal distances from each other."

In a paper entitled "A New Method of Spectrum Observation*," Mr Lockyer regards this spectrum as illustrative and confirmatory of his views regarding the possibility of elemental dissociation at different heat-levels. The view taken by Mr Lockyer may be expressed in his own words:—

"The flame spectrum of magnesium perhaps presents us best with the beautiful effects produced by the passage from the lower to the higher heat-level, and shews the important bearing upon solar physics of the results obtained by this new method of work. In the flame the two least refrangible of the components of *b* are seen associated with a line less refrangible so as to form a triplet. A series of flutings and a line in the blue are also seen. On passing the spark all these but the two components of *b* are abolished. We get the wide triplet replaced by a narrow one of the same form, the two lines of *b* being common to both....

"May we consider the existence of these molecular states as forming a true basis for Dalton's law of multiple proportions? If so, then the metals in different chemical combinations will exist in different molecular groupings, and we shall be able, by spectrum observations, to determine the particular heat-level to which the molecular complexity of the solid metal, induced by chemical affinity, corresponds. Examples.—None of the lines of magnesium special to the flame spectrum are visible in the spectrum of the chloride either when a flame or a spark is employed."

In order to ascertain the true cause of the variations in the magnesium spectrum, the following experiments and observations were made, and they

* *Proc. Roy. Soc.*, Vol. xxx, p. 22.

demonstrate that the views of Mr Lockyer on this question must also be regarded as resting on faulty experimenting:—

1. *Observations on the Spark between Magnesium Points in Nitrogen and Carbonic Oxide at various Pressures.*

The points were pieces of magnesium wire. Round one end of each a platinum wire was tightly coiled and fused into the side of a glass tube. This tube was attached by fusion at one end to another tube filled with phosphoric anhydride, which in turn was connected with a Sprengel pump. The other end of the tube was connected by a thick rubber tube, capable of being closed by a pinch-cock, with a gasholder containing nitrogen over strong sulphuric acid. The tube, having been exhausted and filled with nitrogen two or three times, it was found that no line at 5210 was visible in the spark. The tube was now gradually exhausted, and the spark watched as the exhaustion proceeded. No line at 5210 was seen, although the exhaustion was carried nearly as far as the pump would carry it; nor was any hydrogen line (C or F) visible, either with or without the use of a jar. The communication with the gasholder was now opened, and the tube refilled with nitrogen at the atmospheric pressure; a communication was then made with another vessel containing hydrogen, which was allowed to diffuse into the tube for a very short time. On now passing the spark, the line at 5210 at once appeared, although the quantity of hydrogen diffused into the nitrogen must have been very small. The experiments with nitrogen at reduced pressure were repeated several times, with the same result. It was found necessary to have the phosphoric anhydride, as without it traces of moisture were left or found their way through the pump into the tube, and then, when the exhaustion was carried far enough, both the line at 5210 and the hydrogen lines, C and F, made their appearance. We have never, however, been able to detect the line at 5210, in nitrogen, without being able to detect C or F either at the same time or by merely varying the discharge by means of a Leyden jar.

Experiments made in the same way with carbonic oxide instead of nitrogen led to precisely the same results.

2. *Observations on the Spark between Magnesium Points in Hydrogen at reduced Pressures.*

A tube, similar to those employed with nitrogen and carbonic oxide, was attached at one end to a Sprengel pump and mercury gauge, and at the other end to an apparatus for generating hydrogen. Dry hydrogen was passed through for some time, and the connection with the hydrogen apparatus closed. On sparking with the hydrogen at the atmospheric pressure, the line at 5210 and its attendant series were visible, and were still visible

when a small Leyden jar was used with the induction-coil, but disappeared almost entirely when a large Leyden jar was used. When the pressure of the hydrogen was reduced to half an atmosphere, the line at 5210 was seen faintly when a large Leyden jar was used, but not the series of fine lines. When the pressure was reduced to 180 millims., the series of fine lines began to shew when the large jar was used. By still further reducing the pressure the whole series was permanently visible when the large jar was used; but when the exhaustion was carried still further they grew fainter, and almost disappeared. On gradually readmitting hydrogen, the same phenomena recurred in the reverse order.

3. *Observations on the Arc with Magnesium and Hydrogen.*

The line at 5210 is not seen in the arc in a lime or carbon crucible when magnesium is dropped in without the introduction of hydrogen. If, however, a gentle stream of hydrogen or of coal gas be led in through a perforation in one of the electrodes, the line at 5210 immediately makes its appearance, and, by varying the current of gas, it may be made to appear either bright or reversed. However small the current of hydrogen be made, the line can be detected as long as the current and the supply of magnesium continues, but disappears very quickly when the current of gas ceases.

4. *Observations on the Flame of Burning Magnesium.*

The line at 5210 may often be seen in the flame of magnesium burning in air, but both it and the series of fine lines which accompany it come out with greatly increased brilliance if the burning magnesium be held in a jet of hydrogen, of coal gas, or of steam.

The experiments above described, with nitrogen and carbonic oxide at reduced pressures, are almost if not quite conclusive against the supposition that the line at 5210 is due merely to the lower temperature of the spark in hydrogen. From De La Rue and Müller's observations it would appear that nitrogen at a pressure of 400 millims. should produce much the same effect on the spark as hydrogen at 760 millims. Now the pressures of the nitrogen and carbonic oxide were reduced far below this without any trace of the line in question being visible. Moreover, the magnesium line at 4481, which is not seen in the arc, and may be reasonably ascribed to the higher temperature of the spark, may be seen in the spark at the same time as the line at 5210 when hydrogen is present. Nevertheless temperature does seem to affect the result in some degree, for when a large Leyden jar is used, and the gas is at the atmospheric pressure, the line almost disappears from the spark, to reappear when the pressure is reduced;

but by no variation of temperature have we been able to see the line when hydrogen was carefully excluded.

A line of the same wave-length has been seen by Young in the chromosphere once. Its absence from the Fraunhofer lines leads to the inference that the temperature of the sun is too high (unless at special times and places) for its production. If it be not due to a compound of magnesium with hydrogen, at any rate it occurs with special facility in the presence of hydrogen, and ought to occur in the sun if the temperature were not too high.

We have thus far been careful to ascribe this line and its attendant series to a mixture of magnesium and hydrogen rather than to a chemical compound, because this sufficiently expresses the facts, and we have not yet obtained any independent evidence of the existence of any chemical compound of those elements. We have independent evidence that mixtures which are not probably chemical compounds favour the production of certain vibrations which are not so strong or are not seen at all when the elements of those mixtures are taken separately. The remarkable absorptions produced by mixtures of magnesium with potassium and sodium above-mentioned belong to this class. We have not been able to obtain the emission spectra corresponding to these absorptions, but in the course of our observations on the arc we have frequently noticed that certain lines of metals present in the crucible are only seen, or come out with especial brilliance, when some other metal is introduced. This is the case with some groups of calcium lines which are not seen, or are barely visible, in the arc in a lime crucible, and come out with great brilliance on the introduction of a fragment of iron, but are not developed by other metals such as tin.

Spark Spectrum of Magnesium in Hydrogen under increased Pressures.

In order to ascertain if this peculiar spectrum could be produced at a high temperature in the presence of hydrogen, which we have already shewn to be essential to its production at the atmospheric and at reduced pressures, experiments were made with hydrogen at pressures increasing up to twenty atmospheres.

On the supposition that this spectrum originates from the formation of some chemical compound, probably formed within certain limits of temperature when vapour of magnesium is in presence of hydrogen, the stability of the body ought to depend largely on the pressure of the gaseous medium. Like Graham's hydrogenium, this body might be formed in hydrogen of high pressure at a temperature at which it would under less pressure be decomposed. In fact, it has been shewn by Troost that the hydrides of palladium, sodium, and potassium all follow strictly the laws of chemical

dissociation enunciated by Deville; and increased pressure, by rendering the compound more stable, ought, if the secondary effect of such pressure in causing a higher temperature in the electric discharge were not overpowering, to conduce to a more continuous and brilliant spectrum of the compound. Conversely, if such a more continuous and brilliant spectrum be found to result, in spite of the higher temperature, from increased pressure, it can only be explained by the stability of the substance being increased with the pressure.

Now, what are the facts? When the spark of an induction-coil, without a Leyden jar, is passed between magnesium electrodes in hydrogen at atmospheric pressure, the flutings in the green are, as before described, always seen, but they are much stronger at the poles and do not always extend quite across the field. As the pressure is increased, however, they increase in brilliance and soon extend persistently from pole to pole, and go on increasing in intensity, until, at fifteen and twenty atmospheres, they are fully equal in brilliance to the *b* group, notwithstanding the increased brightness these have acquired by the higher temperature, due to the increased pressure. The second set of flutings, those in the yellowish green, come out as the pressure is increased, and, in fact, at twenty atmospheres only the *b* group and the flutings are noticeable; if the yellow magnesium line be visible at all it is quite lost in the brilliance of the yellow flutings. The tail of fine lines of these flutings extends at the high pressure quite up to the green, and those of the green flutings quite up to the blue. On again letting down the pressure the like phenomena occur in the reverse order, but the brilliance of the flutings does not diminish so rapidly as it had increased. If, now, when the pressure has again reached that of the atmosphere, a large Leyden jar be interposed in the circuit, on passing the spark the flutings are still seen quite bright, and they continue to be seen with gradually diminishing intensity until the sparks have been continued for a considerable time. It appears that the compound, which had been formed in large quantity by the spark without jar at the higher pressures, is only gradually decomposed, and not re-formed, by the high temperature of the spark with jar. This experiment, which was several times repeated, is conclusive against the supposition that the flutings are merely due to a lower temperature. When the pressure was increased at the same time that the jar was employed, the flutings did not immediately disappear, but the expansion of the magnesium lines and the increase of the continuous spectrum seemed to overpower them.

When nitrogen was substituted for hydrogen, the strongest lines of the green flutings were seen when the spark without jar was first passed at atmospheric pressure, probably from hydrogen occluded, as it usually is, in the magnesium electrodes. As the pressure was increased they

speedily disappeared entirely, and were not again seen either at high or low pressures.

With carbonic oxide the same thing occurred as with nitrogen; but in this gas the flutings due to the oxide of magnesium (wave-length 4930 to 5000) were, for a time, very well seen.

Fig. 4 in the plate opposite p. 132 shews more completely than we have given it before the general character of the magnesium-hydrogen spectrum, which consists of two sets of flutings closely resembling in character the hydrocarbon flutings, each fluting consisting of a multitude of fine lines closely set on the less refrangible side, and becoming wider apart and weaker towards the more refrangible side, but extending under favourable circumstances much farther than is shewn in the figure. The set in the green is the stronger, and it was to this that our former observations were confined. It has two flutings, one beginning at about wave-length 5210 and the other close to b_1 on its more refrangible side. The other set consists of three principal flutings, of which the first begins at about wave-length 5618, the next at about wave-length 5566, and the third begins with three strong lines at about the wave-lengths 5513, 5512, 5511. Both sets are very well seen when a magnesium wire is burnt in the edge of a hydrogen flame, and in the arc in a crucible of magnesia when a gentle current of hydrogen is led into it. There is also a pair of bands in the blue beginning at about the wave-lengths 4850, 4802.

Mr Lockyer states (*loc. cit.*) that none of the lines of magnesium, special to the flame spectrum, are visible in the spectrum of the chloride, either when flame or spark is employed. But we find that when the spark is taken between platinum points, from a solution of the chloride of magnesium, in a tube such as those used by Delachanal and Mermet, the line at wave-length 5210 can frequently be seen in it when the tube is filled with air, and that if the tube be filled with hydrogen the green flutings of magnesium-hydrogen are persistent and strong.

Repeated observations have confirmed our previous statements as to the facility with which the magnesium-hydrogen spectrum can be produced in the arc by the help of a current of the gas. In a magnesia crucible, by regulating the current of hydrogen, the flutings can be easily obtained either bright or reversed.

The variations in the spectrum of magnesium, and the conditions under which it is observed, throw additional light on the question of the emissive power for radiation of short wave-lengths of substances at the temperature of flames to which we alluded in our paper on the spectrum of water*.

* *Supra*, p. 116.

Ultra-violet Spectrum of the Flame of Burning Magnesium.

When magnesium wire or ribbon is burnt in air, we see the three lines of the *b* group, the blue line about wave-length 4570, first noticed by us in the spark spectrum*; and photographs shew, besides, the well-known triplet in the ultra-violet between the solar lines K and L sharply defined, and the line for which Cornu has found the wave-length 2850 very much expanded and strongly reversed. These lines are all common to the flame, arc, and spark spectra; and the last of them (2850) seems to be by far the strongest line both in the flame and arc, and is one of the strongest in the spark. But, in addition to these lines, the photographs of the flame shew a very strong, somewhat diffuse, triplet, generally resembling the other magnesium triplets in the relative position of its components, close to the solar line M; and a group of bands below it extending beyond the triplet near L. These bands have, for the most part, each one sharply defined edge, but fade away on the other side; but the diffuse edges are not all turned towards the same side of the spectrum. The positions of the sharp edges of these bands, and of the strong triplet near M, are shewn in the lower part of Fig. 1, p. 132. It is remarkable that the triplets near P and S are absent from the flame spectrum, and that the strong triplet near M is not represented at all either in the arc or spark. The hydrogen-magnesium series of lines, beginning at a wave-length about 5210, are also seen sometimes, as already described by us†, in the spectrum of the flame; but we have never observed that the appearance of these lines, or of the strong line with which they begin, is connected with the non-appearance of b_4 . Indeed, we can almost always see all three lines of the *b* group in the flame, though as b_4 is the least strong of the three, it is likely to be most easily overpowered by the continuous spectrum of the flame.

Burning magnesium in oxygen instead of atmospheric air does not bring out any additional lines; on the contrary, the continuous spectrum from the magnesia overpowers the line spectrum, and makes it more difficult of observation.

Magnesia heated in the oxy-hydrogen jet does not appear to give the lines seen in the flame, except that at 2850.

Spectrum of the Arc.

The spectrum of magnesium, as seen in the arc, contains several lines besides those heretofore described. These lines come out brightly, generally considerably expanded, when a fragment of magnesium is dropped into the crucible through which the arc is passing, but rapidly contract and gradually become very faint or disappear entirely.

* *Supra*, p. 14.

† *Supra*, p. 81.

By examining the arc of a Siemens machine, taken in a crucible of dense magnesia under the dispersion of the spectrum of the fourth order, given by a Rutherford grating of 17,296 lines to the inch, we are able to separate the iron and magnesium lines which form the very close pair b_4 of the solar spectrum. Either of the two lines can be rendered the more prominent of the pair at will, by introducing iron or magnesium into the crucible. The less refrangible line of the pair is thus seen to be due to iron, the more refrangible to magnesium. Comparison of the solar line and the spark between magnesium points confirms this conclusion, that the magnesium line is the more refrangible of the two.

In the ultra-violet part of the spectrum photographs shew several new lines. First, a triplet of lines above U at wave-lengths about 2942, 2938.5, 2937. These lines are a little below a pair of lines given by the spark for which Cornu has found the wave-lengths 2934.9, 2926.7. The latter pair are not seen at all in photographs of the arc, nor the former three in those of the spark. The strong line, wave-length about 2850, is always seen, very frequently reversed. Of the quadruple group in the spark to which Cornu has assigned the wave-lengths 2801.3, 2797.1, 2794.5, and 2789.9, the first and third are strongly developed in the arc, the other two hardly at all. Next follows a set of five nearly equidistant lines, well-defined and strong, but much less strong than the two previously mentioned, wave-lengths about 2782.2, 2780.7, 2779.5, 2778.2, 2776.9. The middle line is a little stronger than the others. The same lines come out in the spark.

Beyond these follow a series of pairs and triplets; probably they are triplets in every case; but the third, most refrangible, line of the triplets is the weakest, and has not in every case been noticed as yet. These succeed one another at decreasing intervals with diminishing strength, and are alternately sharp and diffuse, the diffuse triplets being the strongest. The positions are shewn in Fig. 2, p. 132. The series resembles in general character the sodium and the potassium series described by us in a former communication, and we cannot resist the inference that they must be harmonically related, though they do not follow a simple harmonic law. The most refrangible line in the figure at wave-length 2605 represents a faint diffuse band which is not resolvable into lines; it belongs, no doubt, to the diffuse members of the series, and, to complete the series, there should be another sharp group between it and the line at wave-length 2630. This belonging to the weaker members of the series is too weak to be seen.

It is worthy of remark that the line at wave-length 5710, described by us in a previous communication*, is very nearly the octave of the strong

* *Supra*, p. 82.

line at 2850. Moreover, the measures we have taken of the wave-length of this last line, with a Rutherford grating of 17,296 lines to the inch, indicate a wave-length 2852 nearly, which is still closer to the half of 5710.

When metallic magnesium is dropped into a crucible of magnesia or lime through which the arc is passing, the electric current seems sometimes to be conducted chiefly or entirely by the vaporised metal, so that the lines of other metals almost or wholly disappear; but the line at wave-length 3278* does not in such cases appear, though the other magnesium lines are very strongly developed. The line at wave-length 2850 is often, under such circumstances, enormously expanded and reversed, those at wave-lengths 2801, 2794, and the alternate diffuse triplets, including those near L and near S, much expanded and reversed, and the group of five lines (2776—2782) sometimes reversed.

When the arc of a Siemens machine is taken in a magnesia crucible, the strong line of the flame spectrum, wave-length 4570, is well seen sharply defined; it comes out strongly and a little expanded on dropping in a fragment of magnesium. When a gentle stream of hydrogen is led in through a hollow pole, this line is frequently reversed as a sharp black line on a continuous background. From comparing the position of this line with those of the titanium lines in its neighbourhood, produced by putting some titanite oxide into the crucible, we have little doubt that it is identical with the solar line 4570.9 of Ångström.

When the arc is taken in a crucible into which the air has access, it may be assumed that the atmosphere about the arc is a mixture of nitrogen and carbonic oxide. When a stream of hydrogen is passed, either through a perforated pole or by a separate opening, into the crucible, the general effect is to shorten the length to which the arc can be drawn out, increase the relative intensity of the continuous spectrum, and diminish the intensity of the metallic lines. Thus, with a very gentle stream of hydrogen in the magnesia crucible, most of the metallic lines, except the strongest and those of magnesium, disappear. Those lines which remain are sometimes reversed; those at wave-length 2850 and the triplet near L being always so. With a stronger stream the lines of magnesium also disappear, the *b* triplet being the last in that neighbourhood to go, and *b*₁ and *b*₂ remaining after *b*₄ has disappeared.

Chlorine seems to have an opposite effect to hydrogen, generally intensifying the metallic lines, at least those of the less volatile metals, but it does not sensibly affect the spectrum of magnesium. Nitrous oxide produces no marked effect; coal-gas acts much as hydrogen.

* Ascribed to magnesium in Cornu's map of the ultra-violet solar spectrum.

Spectrum of the Magnesium Spark, in Gases under High Pressures.

In the spark of an induction-coil taken between magnesium points in air we get all the lines seen in the arc except two blue lines at wave-lengths 4350 and 4166, three lines above U, and the series of triplets more refrangible than the quintuple group about wave-length 2780. The blue line wave-length about 4570 is best seen in the spark without a jar when the magnesium electrodes are close together, and the rheotome made to work slowly; and this and the other faint lines of the spark at about 4586 and 4808 require for their detection a spectroscope in which the loss of light is small.

On the other hand, some additional lines are seen. Of these, the strong line at wave-length 4481 and the weaker line at 4586 are well known. Another faint line in the blue at wave-length 4808 has been observed by us in the spark, and two diffuse pairs between H and the triplet near L. Two ultra-violet lines at wave-lengths 2934·9, 2926·7 (Cornu) are near, but not identical with, two lines of the arc above-mentioned; and two more lines at wave-lengths 2797·1, 2789·9 (Cornu) make a quadruple group with the very strong pair conspicuous in the arc in this region. The spectrum of the spark ends, so far as we have observed, with the quintuple group (2782—2776) already described in the arc.

When a Leyden jar is used with the coil, some of the lines are reversed. This is notably the case with the triplet near L, the line at wave-length 2850, and those at 2801 and 2794. Cornu* noticed the reversal of the two less refrangible lines of the triplet near L under these circumstances. This effect is very much increased by increasing the pressure of the gas in which the spark is taken. The Cailletet pump is well suited for such experiments. The gases used were hydrogen, nitrogen, and carbonic oxide; and the image of the spark was thrown on to the slit of the spectroscope by a lens. In hydrogen, when no Leyden jar was used, the brightness of the yellow and of the blue lines of magnesium, except at first that at wave-length 4570, diminished as the pressure increased; while, on the other hand, the *b* group was decidedly stronger at the higher pressure. The pressure was carried up to 20 atmospheres, and then the magnesium lines in the blue and below almost or entirely disappear, leaving only the *b* group very bright, and the magnesium-hydrogen bands which are described above; even the hydrogen lines F and C were not visible. When a jar was used, the magnesium lines expanded as the pressure was increased; all three lines of the *b* group were expanded and reversed at a pressure of 5 atmospheres; the yellow line, wave-length 5528, was also expanded but

* *Compt. Rend.* (1871), Vol. lxxiii, p. 333.

not reversed; and the line at 4481 became a broad, very diffuse band, but the line at wave-length 4570 was but very little expanded. The expansion both of the *b* group and of the yellow line seemed to be greater on the less refrangible than on the more refrangible side of each line, so that the black line in those which were reversed was not in the middle. When the jar was used, the pressure could not be carried beyond 10 or $12\frac{1}{2}$ atmospheres, as the resistance became then so great that the spark would not pass across the small distance of about 1 millim. between the electrodes. At a pressure of $2\frac{1}{2}$ atmospheres, with a jar, the ultra-violet magnesium triplet near L was very well reversed, and the two pairs of lines on its less refrangible side (shewn in Fig. 3 in the plate opposite p. 132) were expanded into two diffuse bands.

In nitrogen and in carbonic oxide the general effects of increased pressure on the magnesium lines (not the magnesium-hydrogen bands) seemed to be much the same as in hydrogen. Without a jar the blue and yellow lines were enfeebled, and at the higher pressures disappeared, while the *b* group was very brilliant but not much expanded. With the jar all the lines were expanded, and all three lines of the *b* group strongly reversed. The bands of the oxide (wave-length 4930—5009) were not seen at all in hydrogen or nitrogen; they were seen at first in carbonic oxide, but not after the sparking had been continued for some time.

The disappearance of certain lines at increased pressure is in harmony with the observations of Cazin*, who noticed that the banded spectrum of nitrogen, and also the lines, grew fainter as the pressure was increased, and finally disappeared. When a Leyden jar is employed there is a very great increase in the amount of matter volatilized by the spark from the electrodes, as is shewn by the very rapid blackening of the sides of the tube with the deposited metal, and this increase in the amount of metallic vapour may reasonably be supposed to affect the character of the discharge, and conduce to the widening of the lines and the reversal of some of them. Without a jar the amount of matter carried off the electrode also doubtless increases with the pressure and consequent resistance, and may be the cause of the weakening, as Cazin suggests, of the lines of the gas in which the discharge is passed. It is to be noted, moreover, that the disappearance of the hydrogen lines depends, in some degree, on the nearness of the electrodes. The lines C and F which were, as above stated, sometimes invisible in the spark when the electrodes were near, became visible, under circumstances otherwise similar, when the magnesium points had become worn away by the discharge.

* *Phil. Mag.*, 1877, Vol. iv, p. 154.

Comparison of the Spectra.

When we compare the spectra of magnesium in the flame, arc, and spark, we observe that the most persistent line is that at wave-length 2850, which is also the strongest in the flame and arc, and one of the strongest in the spark. The intensity of the radiation of magnesium at this wave-length is witnessed by the fact that this line is always reversed in the flame as well as in the arc when metallic magnesium is introduced into it, and in the spark between magnesium electrodes when a Leyden jar is used. It is equally remarkable for its power of expansion. In the flame it is a broad band, and equally so in the arc when magnesium is freshly introduced, but fines down to a narrow line as the metal evaporates.

Almost equal in persistence are the series of triplets. Only the least refrangible pair of these triplets are seen in the flame, another pair are seen in the spark, but the complete series is only seen in the arc. We regard the triplets as a series of harmonics, and to account for the whole series being seen only in the arc we must look to some other cause than the temperature. This will probably be found in the greater mass of the incandescent matter contained in the crucible in which the arc was observed.

The blue line of the flame at wave-length 4570 is well seen in the arc, and is easily reversed, but is always a sharp line, increased in brightness but not sensibly expanded by putting magnesium into the crucible. In the spark, at atmospheric pressure, it is only seen close to the pole or crossing the field in occasional flashes; but seems to come out more decidedly at rather higher pressures, at least in hydrogen.

The series of bands near L, well developed in the flame, but not seen at all in the arc or spark, look very much like the spectrum of a compound, but we have not been able to trace them to any particular combination. Sparks in air, nitrogen, and hydrogen have alike failed to produce them. The very strong, rather diffuse triplet at M, with which they end, so closely resembles in general character the other magnesium triplets, that it may well be connected with that constitution of the magnesian particle which gives rise to the triple sets of vibrations in other cases, but, if so, its presence in the flame alone is not easily explained.

The occurrence of this triplet in the ultra-violet, and of the remarkable series of bands associated with it, as well as the extraordinary intensity of the still more refrangible line at wave-length 2850, which is strongly reversed in the spectrum of the flame, corroborates what the discovery of the ultra-violet spectrum of water had revealed, that at the temperature of flame substances while giving in the less refrangible part of the spectrum more or less continuous radiation, may still give, in the regions of shorter wave-

length, highly discontinuous spectra, such as have formerly been deemed characteristic of the highest temperatures. This subject we will not discuss further at present, but simply remark that "it opens up questions as to the emissive power for radiation of short wave-length of gaseous bodies at the comparatively low temperature of flame with regard to which we are accumulating facts."

In the arc and spark, but not in the flame, we have next a very striking group of two very strong lines at wave-lengths about 2801 and 2794, and a quintuple group of strong but sharp lines above them. The former are usually reversed in the spark with jar, and all are reversed in the arc when much magnesium is present. There are also several single lines in the visible part of the spectrum common to the arc and spark. All of these may be lines developed by the high temperature of the arc and spark. Two blue lines in the arc have not been traced in the spark, but their non-appearance may be due to the same cause as that above suggested for the non-appearance of the higher triplets, the smallness of the incandescent mass in the spark.

A triplet of lines in the arc near U appear to be represented in the spark by an equally strong, or stronger, pair near but not identical in position. The possibility of such a shift, affecting these two lines only in the whole spectrum and affecting them unequally, must in the present state of our knowledge be very much a matter of speculation. Perhaps sufficient attention has not hitherto been directed to the probability of vibrations being set up directly by the electric discharge independently of the secondary action of elevation of temperature. Some of the observations above described, and many others well known, indicate a selective action by which an electric discharge lights up certain kinds of matter in its path to the exclusion of others; and it is possible that in the case of vibrations which are not those most easily assumed by the particles of magnesium, the character of the impulse may slightly affect the period of vibration. The fact that, so far as observations go, the shift in the case of this pair of magnesium lines is definite and constant, militates against the supposition suggested. On the other hand, the ghost-like pairs of lines observed in the spark below the triplet near L, suggest the idea that some of the particles have their tones flattened by some such cause.

The strong pair at wave-lengths 2801, 2794 are accompanied in the spark, but not usually in the arc, by a much feebler, slightly more refrangible pair, but these have not the diffuse ghost-like character of those just alluded to.

These lines are phenomena of the high potential discharge in which particles are torn off the electrodes with great violence and may well be

thrown into a state of vibration which they will not assume by mere elevation of temperature.

There are two lines in the spark besides the well-known line at wave-length 4481 which have not been observed in the arc, but they are feeble and would be insignificant if it were not the fact that they, as well as the line at wave-length 4481, all short lines seen generally only about the poles, appear to be present in the solar spectrum. In the sun we seem to have all the lines common to the flame, arc, and spark, and possibly the strong triplet of the flame at M. We have noticed that when the spark is taken in hydrogen, the line at wave-length 4570 appears stronger than that at wave-length 4703, while the reverse is the case when the atmosphere is nitrogen. It is possible then that the atmosphere may, besides the resistance it offers to the discharge, in some degree affect the vibrations of the metallic particles.

The substantive result of the investigation is to prove that the chemical atoms of magnesium are capable of taking up a great variety of vibrations, and by mutual action on each other, or on particles of matter of other kinds, give rise to a great variety of vibrations of the luminiferous ether; and to trace satisfactorily the precise connection between the occurrence of the various vibrations and the circumstances under which they occur, will require an extended series of observations.

On the Spectrum of Water.

In our observations "On the Spectra of the Compounds of Carbon" (*supra*, p. 103), we noticed that a remarkable series of lines, extending over the region between the lines S and R of the solar spectrum, were developed in the flame of coal-gas burning in oxygen*. The arrangement of lines and bands, of which this spectrum consists, is shewn in Fig. 1, p. 115. It begins at the more refrangible end with two strong bands, with wave-lengths about 3062, 3068, and extends up to about the wave-length 3210. It is well developed in the flame of hydrogen as well as of hydrocarbons, burning in oxygen, and less strongly in the flames of non-hydrogenous gases, such as carbonic oxide and cyanogen, if burnt in moist oxygen. The same spectrum is given by the electric spark taken, without condenser, in moist hydrogen, oxygen, nitrogen, and carbonic acid gas, but it disappears if the gas and apparatus be thoroughly dried. We are led to the conclusion that the spectrum is that of water. The figure is a general view of this spectrum. It was necessary to pass a current of dry gas for fully an hour through the

* This we recorded in a Note of date June 8, 1880, see *Proc. Roy. Soc.*, Vol. xxx, p. 498. Dr Huggins discovered the same spectrum independently, and communicated the same on June 16, 1880. Our paper on this special spectrum bears date 17th June. Both papers were read at the same meeting of the Society.

warmed sparking apparatus before the moisture was sufficiently absorbed by the dehydrating agents. When this was done, photographs of the spark shewed either no trace, or only the faintest traces, of the spectrum above described. On introducing a drop of water, and letting it spread over a plug of asbestos placed in the current of gas, the spectrum above described at once imprinted itself on the photographic plate. The effect was the same, whether the gas used was hydrogen, oxygen, nitrogen, or carbonic acid. In the case of nitrogen, some of the channelled bands due to that gas overlap the water spectrum, and partly obscure it, but not so much but that it can be still very distinctly recognised. When a condenser is used, the water spectrum disappears. The same spectrum appears in the De Meritens arc, but is less fully developed. The spectrum we have figured does not by any means exhaust the ultra-violet spectra of the flames we have observed. In writing of this and other spectra which we have traced to compounds, we abstain from speculating upon the particular molecular condition or stage of combination or decomposition which may give rise to such spectra. The fact of an ultra-violet spectrum of water occurring in spectra of flames opens up questions as to the emissive power for radiation of short wave-lengths of gaseous substances at comparatively low temperatures.

Such facts completely modify the inferences which have been drawn as to the continuity of flame spectra and the character of the specific absorption of the vapour of water.

Identity of Spectral Lines.

In Kirchhoff's *Researches on the Spectra of the Chemical Elements*, p. 10, the following reference is made to the apparent identity of wave-length of some spectral lines.

"If we compare the spectra of the different metals with each other several of the bright lines appear to coincide. This is especially noticeable in the case of an iron and magnesium line at 1655.6 (b_4), and with an iron line and calcium line at 1522.7 (E). It seems to me to be a question of great interest to determine, whether these and other similar coincidences are real or only apparent; whether the lines in question actually fall one upon the other, or whether they lie very close together. I believe that my method of observation does not possess the requisite accuracy for the purpose of answering this question with any degree of probability, and I think that a large number of prisms and an increased intensity of light will prove necessary."

The subsequent investigations of Ångström and Thalén increased the number of apparent coincidences amongst the spectral lines of different elements.

The question of the identity of spectral lines exhibited by different elements is one of great interest, because it is very improbable that any single molecule should be capable of taking up all the immense variety of vibrations indicated by the complex spectrum of iron or that of titanium, and it might therefore be expected that such substances consist of heterogeneous molecules, and that some molecules of the same kind as occur in these metals should occur in more than one of the supposed elements. Further, the supposed identity of certain lines in the spectra of more than one element has been made by Mr Lockyer the ground of an argument in support of a theory as to the dissociation of chemical elements into still simpler constituents, and in reference to this he wrote*: "The 'basic' lines recorded by Thalén will require special study, with a view to determine whether their existence in different spectra can be explained or not on the supposition that they represent the vibrations of forms, which, at an early stage of the planet's history, entered into combination with other forms, differing in proximate origin, to produce different 'elements.'"

Young, on examining with a spectroscope of high dispersion the 70 lines given in Ångström's map as common to two or more substances, has found that 56 are double or treble, 7 more doubtful, and only 7 appear definitely single, and he remarks†: "The complete investigation of the matter requires that the bright line spectra of the metals in question should be confronted with each other and with the solar spectrum under enormous dispersive power, in order that we may determine which of the components of each double line belongs to one and which to the other element." It is this confronting of the bright line spectra of some of the terrestrial elements which we have attempted, and of which we now give an account. For the dispersion we have used a reflecting grating similar to that used by Young, with 17,296 lines to the inch, and a ruled surface of about $3\frac{1}{2}$ square inches; telescope and collimator, each with an aperture of $1\frac{1}{2}$ inch and focal length 18 inches, the lenses being of quartz, cut perpendicularly to the axis and unachromatised, giving a very good definition with monochromatic light. The chromatic aberration is in this case an advantage, for when the telescope is in focus for lines in the spectrum of any given order, the overlapping parts of spectra of different orders are out of focus, and their brightness consequently more or less enfeebled. We have sometimes used green or blue glasses to enhance this result. The telescope and the collimator were generally fixed at about 45° , the collimator being more nearly normal to the grating than the telescope, and the grating moved to bring in successive parts of the spectra. For the parts of the spectra less refrangible than the Fraunhofer line E the

* *Proc. Roy. Soc.*, Vol. xxx, p. 31.

† *American Journal of Science*, Vol. xx, p. 355.

spectrum of the third order was employed, for the more refrangible rays that of the fourth order. The source of light was the electric arc taken in a crucible of magnesia or lime, the image of the arc being focussed on the slit; and, for the examination of any supposed coincidence, first one metal was introduced into the crucible, and the line to be observed placed on the pointer of the eye-piece; the second metal was then introduced, and then in most cases, as detailed below, *two* lines were seen where only one was visible before, and the pointer indicated which of the two belonged to the metal first introduced. In some cases where both metals were already in the crucible, we had to reinforce the spectrum of one of the metals by the introduction of more of that metal, which generally brought out the spectrum of that metal more markedly than the other, and enabled us to distinguish the lines with a high degree of probability. Thus the crucibles of magnesia, or the carbons, always contain sufficient lithium to shew the orange line and the calcium line heretofore supposed coincident with it (wave-length 6101·9), but we observed these lines quite distinct and separated by a distance, estimated by the eye in comparison with the distance of neighbouring titanium lines, at about one division of Ångström's scale. On dropping a minute piece of lithium carbonate into the crucible, the less refrangible line was seen to expand and for a short time to be reversed, the other line remaining narrow and quite unaltered. When the lithium had evaporated, and both lines were again narrow, a small piece of Iceland spar was dropped into the crucible, which immediately caused the expansion, and on one occasion the reversal, of the more refrangible line, while now the less refrangible line was unaffected.

In this way we satisfied ourselves that the calcium line is the more refrangible of the two, and is probably represented by the line at wave-length 6101·9 in Ångström's normal solar spectrum, while the lithium line appears to be unrepresented.

In the case of iron, which gives such a multitude of lines, it was *à priori* probable that some lines would be coincident, or nearly so, with lines of other elements; and in fact we find that in five-sixths of the supposed coincidences lines of iron are involved. We have, therefore, chiefly directed our attention to iron lines. A complete account of the separate resolutions will be found above, pp. 135 to 139.

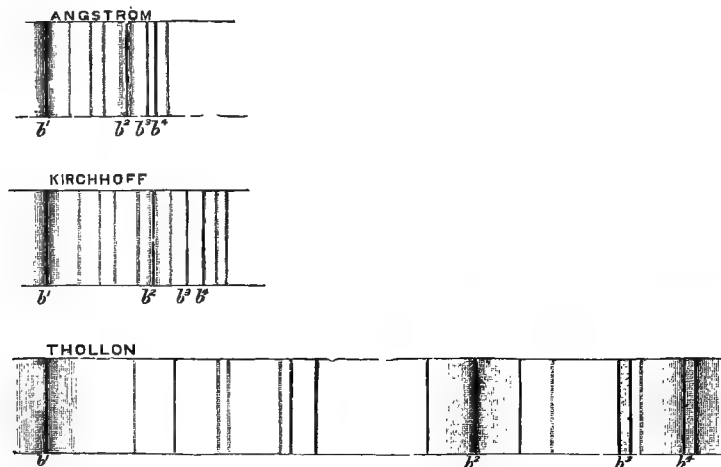
The adjoining figure shews the appearance of the magnesium group of the solar spectrum as observed in spectroscopes used by different observers. The lines marked b^3 and b^4 , which appear to be single lines in the maps of Ångström and Kirchhoff, are resolved into double lines by the greater dispersion employed by Thollon. The following table shews the relative dispersion and number of lines seen by different observers when powerful instruments are directed to the same solar group:—

GROUP E OF SOLAR SYSTEM.

		Number of Lines		Dispersion
Ångström	...	11	...	800
Kirchhoff	...	12	...	1400
Pickering	...	29	...	2000
Young	...	36	...	2720

The indium line 4101.2 we found very difficult to separate from the hydrogen line (*h*), as the latter had to be observed from a tube with a spark, and it is both faint and diffuse; but several observations all led to the conclusion that the indium line is very slightly less refrangible than that of hydrogen.

We have also directly compared the iron line at 5316.07 with the solar spectrum, and found that the iron line corresponds with the less refrangible of the two solar lines at this place, so that the chromospheric line is in all probability the other line of the pair.



The "b" group in the solar spectrum.

There are still a few cases of supposed coincidences which we have not examined. The results which we have recorded strongly confirm Young's observations, and leave, we think, little doubt that the few as yet unresolved coincidences either will yield to a higher dispersion, or are merely accidental. It would indeed be strange if, amongst all the variety of chemical elements and the still greater variety of vibrations which some of them are capable of taking up, there were no two which could take up vibrations of the same period. We certainly should have supposed that substances like iron and titanium, with such a large number of lines, must each consist of more than one kind of molecule, and that not single lines, but several lines of each, would be found repeated in the spectra of some

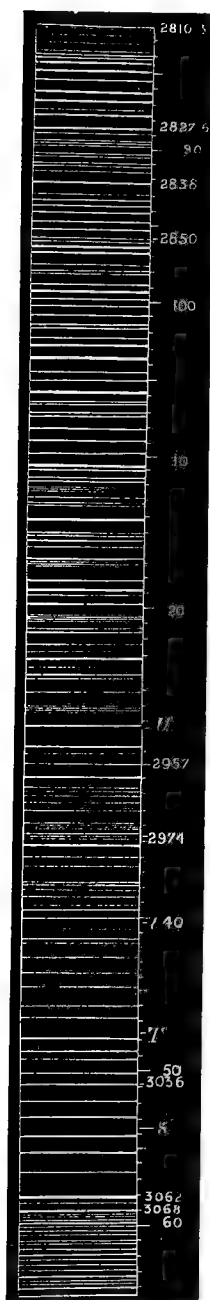
other chemical elements. The fact that hardly single coincidences can be established for any pair of elements, is a strong argument that the materials of iron and titanium, even if they be not homogeneous, are still different from those of other chemical elements. The supposition that the different elements may be resolved into simple constituents, or into a single one, has long been a favourite speculation with chemists; but however probable this hypothesis may appear *à priori*, it must be acknowledged that the facts derived from the most powerful method of analytical investigation yet devised give it scant support.

ON THE SPECTRUM OF WATER. No. II

[*Proceedings of the Royal Society*, Vol. XXXIII. (1882), pp. 274 sqq.]

IN our former communication on the subject of the water spectrum (*supra*, p. 115) we stated that the spectrum we then figured did not by any means exhaust the spectra of flames we had observed, but it was as much as we had at that time been able to trace to water as its cause. We had, in fact, noticed in the spectrum of coal-gas and hydrogen-flames a still more refrangible but less intense series of lines; and we have since observed that this second series is produced under the same circumstances as the first, and we therefore ascribe it to the same cause, namely, the incandescent vapour of water. It is easily produced not only by the flames just mentioned, but by the arc of a De Meritens machine when a current of steam is passed into it, and by the spark of an induction-coil without jar in moist air or other moist gas. When a large coil and jar are used it almost or wholly disappears.

The accompanying figure is drawn from a photograph of the spectrum of an oxy-hydrogen flame; and the wave-lengths marked on it were derived by interpolation from the wave-lengths of the magnesium and iron lines. The arc of a De Meritens machine taken in a crucible of magnesia gave us, when a current of steam was passed into the crucible, both the water spectrum and the metallic lines on the same plate. The solar lines are marked in the figure in positions held by the corresponding iron lines. These photographs were taken with prisms of Iceland spar. None of our photographs shew any more refrangible rays produced by water within the limit of transparency of Iceland spar, *i.e.* below a wave-length of about 2200.



ON THE SPECTRUM OF CARBON

[*Proceedings of the Royal Society*, Vol. xxxiii. (1882), pp. 403 sqq.]

THE spectroscopic investigations we have communicated to the Society "On the Reversals of the Lines of Metallic Vapours," have shewn the importance of a thorough and accurate knowledge of the ultra-violet spectra of the elements, for it is in the lines of short wave-length as a rule that the greatest emissive power is manifested, and they are therefore most readily reversed. Thus we have succeeded in reversing upwards of 100 lines in the ultra-violet spectrum of iron (*Proc. Roy. Soc.*, Vol. xxxii, p. 404). The necessity for accurate data in regard to this region of the spectrum led us to make a long study of the spectrum of magnesium, and the results of this investigation appeared in the volume of the *Proc. Roy. Soc.* just cited. Having had occasion to examine the origin of the different fluted spectra of carbon, it became apparent that a complete knowledge of the relations of these spectra to the simple spectrum of the element could only be reached by the help of a complete record of the line spectrum. Ångström and Thalén, in their memoir "On the Spectra of the Metalloids" (*Nova Acta Reg. Soc. Upsal.*, Ser. iii, Vol. ix), give a map and table of wave-lengths of the lines due to carbon in the visible part of the spectrum, as distinguished from the fluted spectra given by compounds of carbon, namely, carbonic oxide, cyanogen, and acetylene. These lines, they state, always appeared when very powerful induction sparks were passed through the vapour of any compound of carbon, or between carbon electrodes. This line spectrum is remarkable for simplicity, consisting of eleven lines, of which the single line in the yellow, followed by a triple group in the green, and a very strong line in the blue, recall vividly the spectrum of magnesium; and as we know two modifications of the spectrum of magnesium which seem to be due respectively to the oxide and a hydride, the parallel between the behaviour of the two elements is the more striking. The plates of the ultra-violet spectra of the metals by the late Professor W. A. Miller (*Phil. Trans.*, 1864) include plates of the spark taken between metallic electrodes in different compounds of carbon, which shew with sufficient clearness that there are some five groups of lines in the ultra-violet spectrum of this element. In the observations

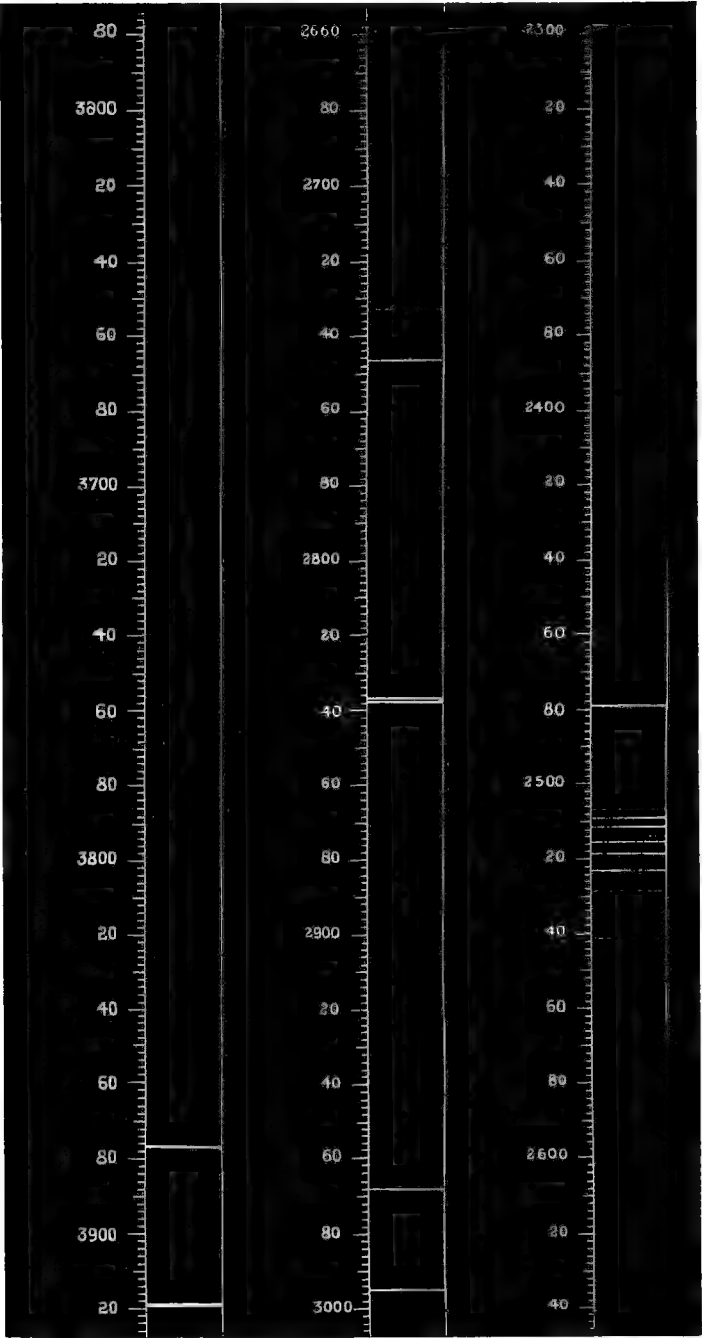
here described we have preferred taking intense induction sparks between pure graphite poles in different gases.

The accompanying figure represents the ultra-violet spectrum of carbon to a scale of wave-lengths within the range of the rays transmitted through calcite. The lines figured have been observed in photographs of the spark of a large induction coil, having a large Leyden jar in connexion with the secondary coil, between poles of purified graphite in air, carbonic acid gas, hydrogen, and coal-gas. The same lines have been observed in photographs of the spark between iron, and between aluminium poles in carbonic acid gas. By comparing the photographs taken under these different circumstances, we have, we believe, eliminated the air lines, which are numerous and strong in the region between H and T, and will form the subject of a future communication, and also the metallic lines which graphite, purified with the utmost care, still exhibited.

The graphite was purified by being stirred in fine powder into fused potash, and subsequent treatment with aqua regia, by prolonged ignition in a current of chlorine, and by treatment with hydrofluoric acid. The well washed powder was afterwards compressed into blocks by hydraulic pressure between platinum plates, and from these blocks the electrodes employed were cut. Notwithstanding the purification the photographs of the spark between these electrodes still shewed very distinctly lines of magnesium and iron. This fact shews the extreme difficulty of getting rid of all impurity, and the caution which is requisite in any reasoning depending on the assumption of chemical purity in the materials employed. It is very possible that the magnesium and even the iron in this case may have been due to oxides of those metals in the floating dust of the laboratory, which we know always contains sodium compounds, and which at Cambridge, where the water, soil, and bricks contain sensible quantities of lithium, almost always shews traces of that element.

The wave-lengths of the strongest carbon lines were determined by means of a Rutherford diffraction grating having 17,296 lines to the inch. The measures were made in the following way: The collimator and telescope of the goniometer were first centred by the instrument maker's marks. The telescope was then more carefully adjusted for centre by directing it on to a distant mark, taking the reading of the circle, turning the arm carrying the telescope through 180° and reversing the telescope, whereby the mark was again brought into the field of view, and adjustments were then made until the mark had the same position on the cross-wires in both positions of the telescope. The grating was next placed in position, and, after adjustment to the vertical plane, was brought very nearly at right angles to the axis of the collimator by turning it until the sodium D lines in the spectra of the second order were observed to fall at equal distances on either side of the collimator.

Ultra-violet Spectrum of Carbon.



The small photographic slide, containing the sensitive plate, fitted the telescope in place of the eye-piece, and so could easily be turned about an axis coincident, or nearly so, with the optic axis of the telescope. In taking a measurement of the position of a line the approximate wave-length was first found by interpolating between the nearest cadmium or other lines of known wave-length in photographs taken with calcite prisms. The telescope was then set to the angle corresponding to this approximate wave-length for the spectrum of the fourth order. The lower half of the slit was closed by a shutter, and the photographic slide having been adjusted for level, the plate was exposed to the light which came through the upper half of the slit, and gave an image of the lines in the lower half of the field. When this exposure was completed, the photographic slide was turned round through 180° about the axis of the telescope, so as to bring to the top that part of the sensitive plate which before had been lowest. It was then exposed a second time, and thus two images of the same line were impressed on the plate, which were necessarily at equal distances on either side of the point where the axis of the telescope met the plate. By a subsequent measurement, with a micrometer under a microscope, of the distance between the two images, and the conversion of this distance into angular measure, a correction was found, which was added to, or subtracted from, the reading of the circle to get the exact deviation of the ray producing the line under observation. Another photograph of the same line was next taken in the same way as before, except that the telescope was placed at the corresponding angle on the other side of the collimator. From the two angles thus found, the wave-length of the line was calculated. The process was repeated three or four times for each line, and the mean wave-lengths thus found for carbon lines were 2296.5, 2478.3, 2509.0, 2511.9, 2836.3, and 2837.2. The numbers deduced from the different photographs of the same line differed from one another in the last figure only, so that we are justified in assuming the first four figures to be accurate in each case. The wave-lengths of the remaining lines were obtained by interpolation from measures of photographs, taken with a train of two calcite prisms of 30° each and one of 60° , on which the iron as well as the carbon lines were shewn. The wave-lengths of the iron lines used in the interpolations were deduced from photographs taken with the grating in the same way as that above described for the carbon lines. The wave-lengths thus found for the remaining carbon lines are given in the table below.

In taking the photographs of the spark, the induction coil was sometimes worked by a De Meritens magneto-electric machine, and in that case the stream of sparks was not only extremely brilliant, but produced a deafening roar. Notwithstanding this character of the spark, the photographs, when the spark was taken in air, between poles of purified graphite, shewed, besides the carbon lines above described, the set of six cyanogen flutings in the blue very distinctly, and those between K and L, and those near N,

strongly developed. On the other hand, when the spark was taken in carbonic acid gas, these flutings almost entirely disappeared, and would no doubt have disappeared entirely, if the last traces of air had been removed from the apparatus.

Table of Carbon Lines.

Authors	Colour	Wave-length	Intensity *
Ångström and Thalén	Red	6583·0	2
		6577·5	1
		5694·1	4
	Orange	5660·9	4
		5646·5	3
		5638·6	5
	Yellow	5379·0	6
	Green	5150·5	4
		5144·2	3
		5133·0	5
	Indigo	4266·0	1, diffuse
Liveing and Dewar	Ultra-violet ...	3919·3	2, diffuse
		3876·5	4, " "
		2995·0	4, very diffuse
		2968·0	5, " "
		2837·2	2
		2836·3	2
		2746·5	3, very diffuse
		2733·2	6, " "
		2640·7	4, " "
		2541·5	6
		2528·2	5
		2523·6	5
		2518·7	5
		2515·8	4
		2514·0	5
		2511·9	2
		2509·0	3
		2506·6	5
		2478·3	1
		2296·5	3

Spectrum of Incandescent Carbon Filaments.

We have also examined the spectrum of Swan's incandescent lamps. So long as the carbon thread is unbroken, it emits a continuous spectrum, on which neither bright nor dark lines are visible. By gradually increasing the number of cells in the battery, until the thread gave way, we found at the instant of fracture, for a small fraction of a second only, that a set of flutings in the green appeared. In some of those lamps we observed, when the

* The scale of intensity here adopted, 1 to 10, is like that used in regard to the magnitude of stars, 1 indicates the brightest, 10 the least bright line.

current was nearly as much as the carbon thread would bear without rupture, that a sort of flame appeared in the lamp. On examining the spectrum of this flame, it gave the flutings of carbonic oxide very distinctly, and we made sure that they were those of carbonic oxide, and not those of hydrocarbons, by comparison with the bands of a Bunsen burner. Closer examination shewed that this flame was strongest about the junction of the carbon thread with one of the conducting wires, and that on reversing the current, it shifted from one wire to the other, and the wire about which it appeared was always the positive electrode. In fact, the flame was the glow of the positive pole attending a discharge in rarefied gas; when the resistance of the carbon thread became too great in proportion to the intensity of the current, the discharge began to occur through the rarefied atmosphere within the envelope of the lamp. The spectrum shewed that this atmosphere contained carbonic oxide.

By interposing different flames between the incandescent lamp and the slit of the spectroscope, we have been able to make some comparisons of the probable temperatures of the flames and filament. For this purpose a lens of 3 inches focal length was placed 6 inches in front of the slit, and an image of a horizontal part of the incandescent carbon thread formed by it across the (vertical) slit. The appearance in the field of view of the spectroscope was a narrow continuous spectrum extending all across the field. When a flame was interposed between the lens and the slit, the bright lines of the flame were seen above and below the narrow continuous spectrum, and in some cases were continued across it, or were seen reversed upon it. When the flame was that of a Bunsen burner in which was a platinum wire with sodium carbonate, the yellow sodium lines were seen bright above and below the continuous spectrum of the carbon thread, but reversed where they crossed it. When lithium was substituted for sodium in the flame, the red lithium line was also seen bright above and below the continuous spectrum, but reversed where it crossed it. When an oxy-hydrogen jet was substituted for the Bunsen burner, and sodium carbonate held in it, the yellow sodium lines were not only bright above and below the continuous spectrum of the carbon, but shewed as bright lines where they crossed it, in fact they were conspicuously brighter than the carbon. When coal-gas was substituted for hydrogen in the jet, the same appearance presented itself, only the sodium lines were not so much brighter than the carbon as they were before. Fifty Grove's cells were used with the incandescent lamp, which were as many as could be used without danger of rupturing the threads. When barium chloride was held in the hydrogen flame fed with only a little oxygen, the bright green line of barium (wave-length 5534) was well seen above and below the continuous spectrum, but could not be traced either bright or dark across it. When a flame of cyanogen burning in air was interposed, the bright bands of that flame could be seen above and below the continuous

spectrum, but could not be traced either bright or dark across it. When sodium carbonate was held in this flame the yellow sodium lines were seen feebly reversed where they crossed the spectrum of the incandescent lamp. We infer from these experiments that the emissive power of the carbon thread for light of the refrangibility of the D lines is nearly balanced by that of sodium at the temperature of the flame of cyanogen burning in air, but is sensibly less than that of sodium, at the temperature of a jet of coal-gas and oxygen, much less than that of sodium in the oxy-hydrogen jet. This seems to render it probable that the temperature of the incandescent thread is not far different from that of a cyanogen flame burning in air (or rather the temperature it conveys to the sodium in it), but is less than that of an oxy-hydrogen flame, though this does not necessarily follow from the experiments, inasmuch as the radiation of the sodium is so much more limited as to range than that of the carbon. When a Bunsen burner or a gas blowpipe flame was interposed between the lens and slit, no reversal of the hydrocarbon bands could be seen. When magnesium was burnt between the lens and slit, the magnesium lines (*b*) were seen bright, eclipsing the carbon. Possibly the smoke of magnesia may have considerably helped to eclipse the light of the carbon.

ON THE DISAPPEARANCE OF SOME SPECTRAL LINES AND
THE VARIATIONS OF METALLIC SPECTRA DUE TO MIXED
VAPOURS

[*Proceedings of the Royal Society*, Vol. XXXIII. (1882), pp. 428 sqq.]

THE theory of spectral lines most commonly received is that the motions of the luminiferous ether producing them are not directly due to any motion of translation of the molecules of the emitting substance, but to relative motions of the parts of the same molecule, or in other words, to vibrations occurring within the molecules; and that the mutual action of the molecules, while it may give rise to irregular vibrations of the ether, affects the regular vibrations producing the lines only in an indirect manner, by converting part of the motions of translation into internal vibrations. On this theory the spectral lines which any given substance can readily take up will in general be limited to a certain number of fundamental lines and a number of others harmonically related to them, though not necessarily simple harmonics of the fundamental lines. And variations of temperature, by altering the rapidity and the violence of the action of one molecule on another, will alter the intensities of the several vibrations, but not their periods, unless the violence should extend to the disintegration of the molecules, which would be equivalent to the formation of new molecules with new fundamental periods of vibration. In view of this theory, the observations on the spectrum of magnesium have a special interest, because from the close analogy of magnesium to zinc and cadmium, it is inferred that the molecules of magnesium vapour are chemical atoms of that substance, that is to say, they pass apparently undivided through all the chemical changes to which magnesium may be subjected; and it seems reasonable to suppose that any subdivision of the chemical atoms could not fail in this case to be attended with a change of chemical qualities, which, in the presence of other elements, would give rise to new compounds. No such new compounds have in fact been detected. We have already described in detail the differences between the spectra of magnesium as seen in the flame of the burning metal, the electric arc, and the spark discharge, and we have now some further observations upon them to place before the Society, which are confirmatory of the received theory.

We have observed the spectrum of a block of magnesia, rendered incandescent by an oxy-hydrogen jet. In the visible part of this spectrum we found no discontinuity, no lines bright or dark (except the inevitable D lines), no sign of the blue channelled spectrum of magnesia. Drs Huggins and Reynolds (*Proc. Roy. Soc.*, Vol. xviii, pp. 547, 551) have recorded the appearance of the *b* group under these circumstances, but we failed to get sight of it. In the ultra-violet region photographs still shew a continuous spectrum, extending far beyond the limit of the solar spectrum, in fact as far as we have hitherto observed any lines of magnesium to occur, but on this continuous spectrum one line, and only one, comes out, which is the strongest line of burning magnesium and of the arc spectrum, at wave-length 2852 (2850 Cornu). This line shews sometimes bright, sometimes reversed, against the continuous background. In this case, where the appearance of the lines depends on their relative brightness, as compared with the continuous spectrum, there is no advantage, so far as the visible rays are concerned, in the photographic method over that of observation by the eye; there may be a disadvantage, as the photograph presents only the mean result of a certain time. But where the faint lines of a discontinuous spectrum are in question the photographic method has the advantage, for when the vibrations are too feeble to produce any sensible impression on the retina, they may yet, by integration of their effects during a lengthened exposure, produce a definite effect on the photographic plate. In general we have only exposed our plates for such times as would give us the best defined images, so that very faint lines are not developed in them; but by using a prolonged exposure we find that in many cases the disappearance of lines from the arc or spark is more apparent than real, and is attributable to a variation of intensity, not to an absolute cessation of the vibrations corresponding to the evanescent lines. Thus of the quadruple group between wave-lengths 2789 and 2802 in the spark spectrum of magnesium only the stronger two lines are usually seen in photographs of the arc with short exposure, but the whole four produce their impressions on the plate if sufficient time be given. Again, the triplet in the arc spectrum at wave-length about 2942—2937·5 is not usually seen in the spectrum of the spark, but when the plate has had a lengthened exposure the stronger two lines of this triplet make their appearance in the spectrum of the spark. Even the triplet near M, so strong in the flame of burning magnesium, but not before recognised either in the arc or spark in photographs taken with short exposure*, comes out in plates of the spectrum of the Spottiswoode induction spark (if we may give this name to the method of stimulating the induction coil by the intermittent current of a magneto-electric machine, see *Proc. Roy. Soc.*, Vol. xxx, p. 175) between magnesium electrodes, which have had four or five minutes' exposure.

* Dr Huggins has informed us that his old photographs of the magnesium spark taken with an induction coil in the ordinary way shew this triplet distinctly.

These observations tend to confirm the theoretical view that alterations of temperature cannot put a stop to any of the fundamental vibrations of a molecule; at the same time we cannot be sure that the impulses communicated by an electric discharge may not be in some respects different from those resulting from mere increment of temperature.

There is, however, a further point for consideration, which is, how far the presence of a mixture of molecules of different elements affects the respective vibrations. This is a condition which obtains in most or all of our observations of the arc in crucibles, as well as in the solar atmosphere, so that it is important to see if any effects can be traced to such a condition of matter. Indeed, in order to arrive at any probable explanation of the variations observed in the spectra of sun-spots and of the chromosphere, we require to study the phenomena produced by such mixtures of vapours as exist in our crucibles, and not merely the spectra produced by the isolated elements, either in arc, spark, or flame.

It is only on some such supposition as that above suggested that we can account for the absorption lines produced by admixtures of magnesium with sodium and potassium respectively (*Proc. Roy. Soc.*, Vol. xxvii, p. 353); and it is possible that the very remarkable effect of hydrogen in producing the reversal of chromium lines (*ib.*, Vol. xxxii, p. 405) and of other lines (*ib.*, Vol. xxviii, p. 472) is a result of analogous action. We have more particularly observed the effect of a current of hydrogen on the iron lines at wave-lengths 4918, 4919·7, and 4923. These lines, as seen in the arc in a magnesia crucible, usually have about the same relative strengths as are shewn in Ångström's map of the solar spectrum; Thalén gives their intensities as 2, 1, 3 respectively. They are all developed simultaneously when iron is dropped into the crucible, the first being sometimes reversed, the second frequently reversed for some time, the third much strengthened but not reversed. After a time these effects die out, but if now a *very gentle* current of hydrogen is led in through one of the carbons perforated for the purpose, the line at 4919·7 is again strongly reversed, that at 4918 expanded, while that at 4923 becomes very bright but remains sharply defined. These effects of the hydrogen were observed several times. In all cases the line at wave-length 4923 seemed to maintain about the same relative strength compared with the other two lines, and never shewed any variation at all corresponding to the prominence it holds in Young's catalogue of chromospheric lines, where it has a frequency of forty, while that at 4918 has only half that frequency, and the strongest line of the three does not figure at all*.

* Mr Lockyer's figure (*Proc. Roy. Soc.*, Vol. xxxii, p. 205) accompanying his paper on the spectra of sun-spots shewing "what happens with regard to three adjacent iron lines under different solar and terrestrial conditions," is at variance with our observations, in so far as the line at 4923 is represented as absent from the arc.

Some further observations on this group of lines are contained in the sequel.

The effects of mixtures of metallic vapours in developing bright lines are equally marked, and in general more easily observed. We have before noticed (*Proc. Roy. Soc.*, Vol. xxx, p. 97) that certain lines of metals present in the crucible "are only seen, or come out with especial brilliance, when some other metal is introduced. This is the case with some groups of calcium lines which are not seen, or barely visible, in the arc in a lime crucible, and come out with great brilliance on the introduction of a fragment of iron, but are not developed by other metals such as tin." Effects of this kind are most frequent in the case of metals which produce a large number of lines. They are specially noticeable in the case of nickel and titanium. Both these metals produce many lines, but a comparatively large quantity of nickel may be introduced into a crucible of magnesia, through which the arc of a powerful Siemens dynamo-electric machine is passing, without the lines of nickel being strongly developed; they shew steadily as sharp but not specially bright lines; but after several other metals—iron, chromium, &c.—have been put in in succession, the nickel lines frequently come out with great brilliance and considerably expanded, and remain so for a long time. The titanium lines are generally very persistent when that metal (as cyanide or oxide) has been introduced into the crucible, but are subject to continual variations of intensity; sometimes they are twinkling, at other times steady; but they can frequently be brought out with great brilliance by dropping in iron or other metals. In such cases the metals put into the arc can hardly be supposed to increase the resistance or the temperature, but they may assist the volatilisation of each other, and may also act by reduction, and so by increasing the incandescent mass strengthen the weaker lines. Chlorides, however, which seem to have the effect of helping the volatilisation and diminishing the resistance so that the arc can be drawn out to a greater length, usually sweep out the fainter lines.

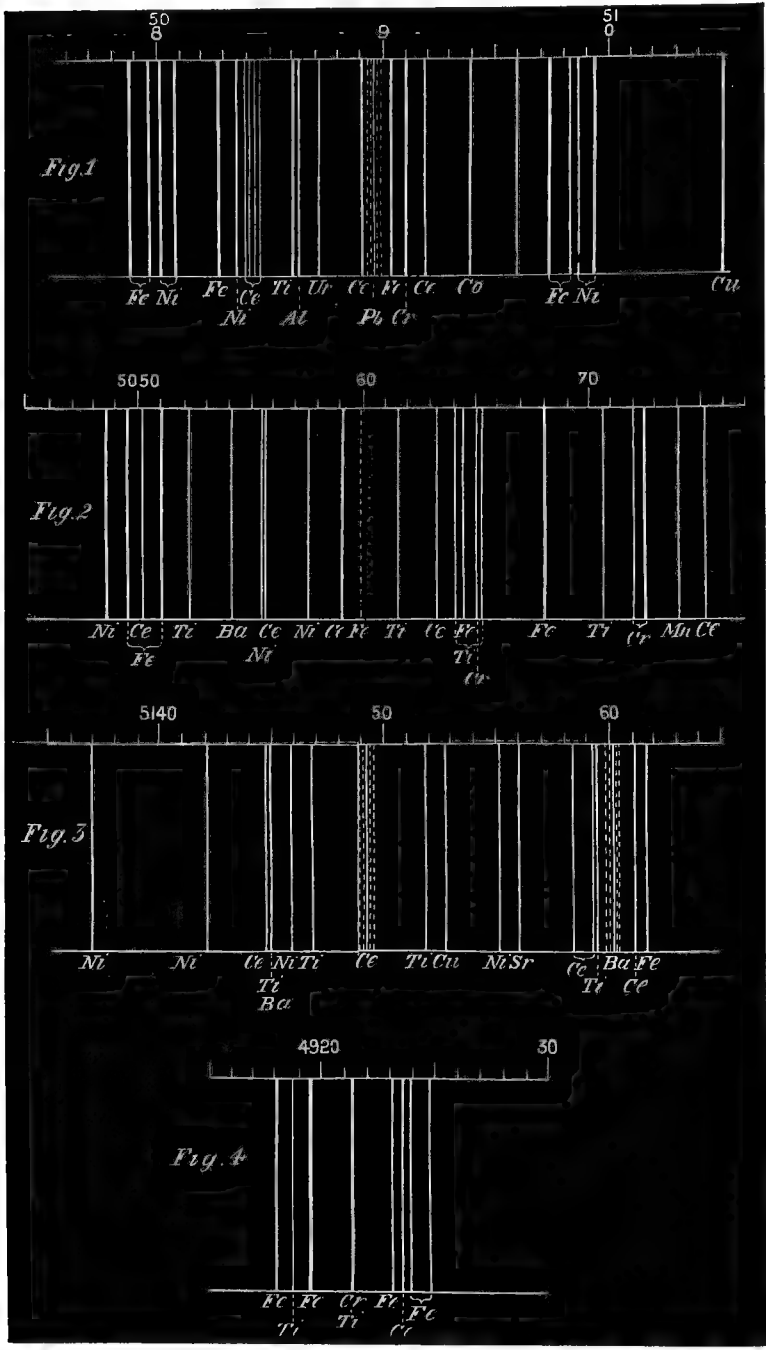
In many cases when a fragment of a metal is dropped into the crucible brilliant lines, hitherto unrecorded, come out for a short time and quickly die out. It is hardly possible in such cases to say without prolonged observations whether these lines belong to the newly introduced metal or to some of those previously put in and developed by the presence of the new metal. How much remains to be done in the study of these lines, and how much light this may throw on the phenomena of the solar lines, will be seen from the following account of our observations of some very small portions of the spectrum of the arc in a magnesia crucible. The portions selected are of special interest, because in these regions a remarkable outburst of broad Fraunhofer lines, not usually visible, is recorded by the Astronomer Royal as having occurred in a sun-spot (*Monthly Not. Ast. Soc.*, 1881).

Fig. 1 shews the principal (not all the) lines which were in the same field of view when the spectrum of the 4th order produced by a Rutherford grating (17,296 lines to the inch) was observed, the light being that of the arc of a Siemens machine in a magnesia crucible. A small piece of copper was first put in and then some nickel, and by the lines of these metals the portion of the spectrum under examination was identified. The iron lines were as usual also present. The symbols affixed to the several lines shew those which came out when the metals indicated were introduced. Thus, when chromium was dropped in, a very brilliant line came out near the middle of the field, a little below the iron line wave-length 5090·4; titanium cyanide brought out a line at about wave-length 5086, cobalt one at 5094, uranic oxide one at 5087, and cerium (which may have contained lanthanum and didymium) a number of lines. These lines were very bright for a second or two, and soon became much less brilliant, but were revived when more of the metal was put in. Lead brought out a very evanescent diffuse band represented in the figure by dotted lines. The distances of the several lines from the extreme nickel lines were measured hastily by a micrometer, and are here reproduced to scale. One line at wave-length 5096, though constantly present, did not seem to be affected by any of the metals introduced. An iron line is indicated on Ångström's map at this place, but the introduction of iron, which expanded the neighbouring line at wave-length 5097·3, had no effect on it. It is remarkable that this region in Ångström's normal solar spectrum is particularly bare of lines, though Vogel gives several faint lines between those marked by Ångström. It is, however, a region in which many lines have been observed in sun-spots (*Greenwich Spectroscopic and Photographic Results*, 1880), and the most prominent of these lines seem to correspond to lines developed by cerium, chromium, and cobalt, though more exact measures than we were able to take at the times that those observations were made are needed in order to establish an exact coincidence.

Fig. 2 represents the lines brought out in a similar way in another short portion of the spectrum, which is also remarkably bare of lines in the solar spectrum.

Fig. 3 shews lines brought out in another place by the several metals indicated. Other lines were visible in this region but were not specially developed by the metals introduced.

The line at wave-length 4923, which occurs so often in the chromosphere, according to Young and Tacchini, and is assumed to be due to iron, is so near to lines which come out in our crucibles on the introduction of other metals, that we cannot help feeling some doubt as to its absolute identification with the iron line; the more so as in Young's catalogue bright lines are sometimes assigned to two metals, of which the real lines differ by nearly a unit of Ångström's scale. This is the case, for example, with the line at



wave-length 5017·6, which is ascribed to iron and nickel. And where lines are broadened, as in sun-spots, the identification with either of two very close lines becomes very difficult.

Fig. 4 shews the lines which come out in the neighbourhood of wave-length 4923. A pair of lines are developed by iron close to this line, and a very bright but evanescent line comes out at about 4923·5, on the introduction of cerium. This is an exceedingly brilliant line for the time, and might easily be mistaken for the iron line unless examined under high dispersion, and it seems to shew that metallic cerium is readily volatile under these conditions. The iron line at 4923 seems to disappear on the addition of titanium, which, on the other hand, brings out the lines marked titanium in the figure. Nickel brings out the cerium line strongly. The line which comes out at 4921·3 on the addition of chromium and titanium is most likely the line seen by Young in the chromosphere thirty times, which up to the present time has not been recognised as due to any element but sulphur.

Both the nickel line at 5016·5 and the adjacent iron line at 5017·5 are seen in the arc in our crucibles, but the nickel line is much the stronger and more persistent. Cerium when put into the crucible brightens the titanium lines, as well as the line at 5017·5. An alloy of manganese, iron, and titanium had the effect of making the nickel line broad and diffuse, without strengthening the 5017·5 line.

These are but samples of the large amount of work which remains to be done before we can pronounce that any of the solar lines are not due to terrestrial elements, or can draw any safe inferences from observed variations in their relative strengths or apparent coincidences; and no real scientific advance can be made by attempting generalisations with the knowledge which we at present possess.

31 AND 32

ON THE ULTRA-VIOLET SPECTRA OF THE ELEMENTS

[*Proceedings of the Royal Society*, Vol. xxxiv. (1882), p. 122.]

PART I. IRON.

(*Abstract.*)

By means of photographs taken with a Rutherford grating of 17,296 lines to the inch, the authors have determined the wave-lengths of ninety-one of the most prominent lines in the spark spectrum of iron between wave-lengths 2948, the termination of Cornu's map of the solar spectrum, and 2327, and also of fourteen of the strongest lines in the spark spectrum of copper beyond that, up to the wave-length 2135. Using these lines as lines of reference they have, from photographs taken with calcite prisms, deduced the wave-lengths of 584 more lines in the arc and spark spectra of iron within those limits. These lines are mapped on the same scale as Ångström's and Cornu's maps of the solar spectrum. The paper describes the method of taking the measures, and gives in detail the quantities observed and the data on which the calculations are founded.

PART II. VARIOUS ELEMENTS OTHER THAN IRON.

(*Abstract.*)

In the second part of this paper the authors have given a map of the ultra-violet lines of potassium, sodium, lithium, barium, strontium, calcium, zinc, mercury, gold, thallium, aluminium, lead, tin, antimony, bismuth, and carbon, as developed in the arc. They point out that in several cases the lines are in all probability harmonically related, as shewn by the repetition of similar groups of lines at regularly diminishing distances, the groups being alternately sharply defined and diffuse, and becoming more diffuse as they die away at the end of the series. They had previously called attention to this kind of relationship between the visible lines in the spectra of the alkalis and of magnesium. The like relationship holds good in the ultra-violet spectra of those metals, and is strongly marked in the cases of calcium and zinc, less strongly in some other metals.

ON THE ULTRA-VIOLET SPECTRA OF THE ELEMENTS

PART I. IRON (WITH A MAP)

[*Philosophical Transactions of the Royal Society*, Vol. 174 (1883),
pp. 187 sqq.]

ÅNGSTRÖM'S "normal solar spectrum" has served most spectroscopists as a standard of reference for wave-lengths in the visible part of the spectrum. Cornu's continuation of it, and particularly the map of the iron lines which he used in the construction of it, serves very well for such a standard up to the limit of the solar spectrum, *i.e.*, to a wave-length 2948 (U). For the region above this we have had to use Mascart's and Cornu's wave-lengths of the cadmium lines, and Cornu's wave-lengths of some magnesium lines. The intervals between those lines are, however, too great for any close approximation to the wave-lengths of intervening lines by interpolation, and, moreover, the wave-lengths did not appear to be determined with sufficient precision to serve as a standard, and the lines are ill adapted to that purpose by reason of their diffuse character. For the determination of the wave-lengths of lines in this higher region we have, therefore, been driven to form a standard for ourselves. For this purpose we have chosen the iron spectrum which had been employed by Cornu in the region which he mapped, and seemed to answer the purpose well, both from the number of lines which it presents and their characteristic grouping by which they may easily be recognised by anyone who has once become familiar with them. The wave-lengths of the most prominent lines were determined by means of a Rutherford diffraction grating, as detailed below, between the wave-lengths 2948 and 2327; but beyond this there is a remarkable falling off in the intensity of the iron lines, and between wave-lengths 2327 and 2135 (which is near the limit of transparency of Iceland spar) we have preferred to determine the wave-lengths of the prominent copper lines which are numerous and strong in that region. The wave-lengths of a series of lines at short intervals having thus been determined, those of the intervening lines were obtained by interpolation, and the result is shewn in the map of the iron spectrum above U which accompanies this paper.

The instruments.

The goniometer used was constructed for us by Hilger, and has a circle of 18 inches diameter, graduated at intervals of 5' by Simms. Fractions of 5' are read by a microscope with a micrometer eye-piece fixed to the arm which carries the telescope.

The telescope and collimator have each an object-glass consisting of a single lens of quartz $1\frac{1}{2}$ inch diameter and a focal length of $18\frac{1}{2}$ inches for the sodium yellow light, but not more than 16 inches for the highest rays measured. The sliding tubes of both telescope and collimator are graduated in fiftieths of an inch, and alterations of focus were made on both instruments at the same time, so that the rays falling on the grating might always be nearly parallel. The graduation of the sliding tube was also used for ascertaining the distance of the photographic plate from the object-glass of the telescope. This was necessary for computing the corrections of the angular measure, as explained below. The collimator is furnished with a quartz lens, of 3 inches focal length, in front of the slit, movable to a greater or less distance, but retained by guides so that its axis may remain coincident with that of the collimator. This lens was placed about 6 inches in front of the slit, and the source of light at the same distance beyond it, so that its image was focussed on the slit.

The measurements were all made by means of photographs taken on Wratten and Wainwright's instantaneous dry gelatine plates. The plates ($2\frac{1}{4}$ inches by 1 inch) were held in a small slide attached to a tube which fitted the telescope in place of the eye-piece, and thus the plate could easily be turned about an axis perpendicular to its plane and coinciding with the axis of the telescope. This turning of the plate about is a matter of no small importance, as it enabled us to avoid the errors which would have arisen from measuring the distances of the lines from the irregular edge of the plate, as will be seen when the mode of measuring the photographs is described. The plates were retained in one position in the slide during exposure by three springs, of which two pressed against two edges of the plate and the other against its back.

The grating was ruled on speculum metal by Chapman with Rutherford's machine, and has a ruled surface of rather more than $1\frac{1}{4}$ inch in each dimension, with 17,296 lines to the inch. It is an excellent grating, but, of course, has the faults which belong to the particular machine by which it was ruled. The definition, when it has not been exposed to variations of temperature, is very good, but it has one inconvenience for our present purpose, which is, that the focus for the same ray in the spectrum of the same order does not fall at quite the same distance from the object-glass of the telescope on the two sides of the normal. The explanation of this has been given by Cornu (*Comptes Rendus*, lxxx, 645), who has shewn that it is

due to a systematic variation in the distance between the ruled lines. As the method employed by us depends upon taking angular measures of the position of the ray on both sides of the normal, and any shift of the focussing tube between the two positions would be likely to introduce serious errors, we have been obliged to be content with the photograph taken on one side being a little, though only a little, less sharp in definition than that taken on the other side. The grating was used with its plane perpendicular to the axis of the collimator, and it was brought into that position in the following way. The telescope and collimator having their axes directed as nearly as possible on to the centre of the circle, the telescope was placed opposite the collimator and the cross wires brought on to the image of the slit, and the reading of the circle taken. The grating was then placed in position and adjusted for level until the spectra occupied the middle of the field of view in all positions of the telescope. It was then adjusted in azimuth until the images of the D lines, from the light of a sodium flame in front of the slit, in the spectra of the second order, on the two sides of the normal were at equal angular distances from the axis of the collimator, as determined by the reading taken when the telescope was opposite the collimator. The grating was then clamped in that position. This adjustment had to be made by hand and was liable to disturbance in the clamping, so that it was afterwards found that the plane of the grating was not quite perpendicular to the axis of the collimator; but as the errors arising from this in the measures on the two sides nearly compensate one another, the final error in the wave-length from this cause is very small indeed.

For measuring the photographs a micrometer was constructed for us by Hilger. This is attached to the stage of a microscope and carries a small frame in which the photographic plate is held by springs. The micrometer-screw has 100 turns to the inch, and by the drum-head $\frac{1}{100}$ th of a turn or $\frac{1}{10000}$ th of an inch can be read. A 1 inch object-glass to the microscope was used, and measures were made by moving the plate until the lines of the photograph were successively bisected by a spider line in the eye-piece. The reading of the micrometer gave the distances between the lines.

The source of light employed was, in the first instance, the arc from a De Meritens magneto-electric machine, in a crucible of magnesia into which iron wire was introduced. But from the overlapping of the spectra of different orders, and the large amount of light emitted by the arc, we found that the plates were so clouded in many places that the lines could not be well seen, and we abandoned the arc for the spark between iron electrodes. This was produced by a large induction coil, worked by five Grove's cells, and having a large Leyden jar connected with the secondary wire. No inconvenience arose from the overlapping of the different orders when the spark was used, because the parts of the spectra of higher and lower orders which overlapped the part of the spectrum of the fourth order to be measured were

always considerably out of focus, the object-glasses of telescope and collimator being uncorrected, and so the light of the lines in the overlapping spectra was diffused and produced only a faint clouding of the plate, which in no way interfered with the measure of the lines of the fourth order.

Mode of proceeding.

The first thing to be done was to obtain a focussing scale for the different angles, including the portion of the spectrum to be mapped. This was already known approximately from Sarasin's table of refractive indices of quartz, and was corrected by a series of trial plates taken at successive angles.

The electrodes, between which the spark was passed, were arranged so that the spark should pass horizontally (the slit being vertical), and at such a height that the visible image formed by the lens in front of the slit on the plates of the slit might fall just above, or partly above, the centre of the slit. The lower half of the slit was closed by a shutter, so that only the lower half of the field of view of the telescope was illuminated. The distance of the spark from the lens had next to be adjusted, as the focal length of the lens for the visible rays is very different from that for the ultra-violet which were to be photographed. This was done by estimation, as there was no need to have the image exactly focussed on the slit, so long as the slit was in the middle of the image and light enough passed through.

The telescope was then set to such an angle as would bring the line to be measured nearly into the centre of the field, the focus adjusted, the photographic slide adjusted and levelled, and the plate exposed. An image of the lines was thus formed on the lower half of the plate. The slide was then turned round through 180° about the axis of the tube, so as to bring what had before been the upper side of the plate to the lower side, and right to left, and again levelled. The plate was then again exposed and thus a second image of the line impressed, and one of the two images was as far to the right of the axis about which the plate had been turned as the other was to the left. Half the distance between the two images would therefore be the distance of the line from the centre of the field, and the knowledge of this would give the means of calculating the deviation of the rays producing the line from the axis of the telescope. The telescope was next turned to the corresponding angle on the other side of the collimator and the operations repeated with a second plate, but without any alterations of adjustment. The telescope was then moved through a small angle, generally $5'$ or $10'$, and the same operations as before repeated on both sides of the collimator, the second pair of plates being intended to serve as a check upon the first.

Similar operations were then repeated at such angular intervals as should bring in the most characteristic strong lines of iron all along the scale.

Beyond the wave-length 2327, it was found that the iron lines were too faint to produce any sufficient impression on the plates. For the region beyond this up to wave-length 2135, copper electrodes were substituted for iron. This being about the limit of transparency of calcite (the material of our prisms), was the limit of our study of spectra at this time.

The measurement of the distance between the two images of a line was made by the micrometer above described, and to convert this distance into arc, it was necessary to know the distance of the plate from the centre of the object-glass of the telescope. It was found by measurement that the distance from the object-glass to the front of the photographic plate, when the sliding tube was at the 100th division, was 439 millims., and the thickness of the lens at its middle 2.5 millims., which, divided by the refractive index of quartz for the high rays observed, is very nearly 1.5 millim., making the distance of the photographic plate from the optical centre of the object-glass very nearly 440.5 millims. From this the formula $\tan^{-1} \frac{D}{3068.5 + 4a}$ was deduced for the angular distance of a line from the axis of the telescope when the difference of the micrometer readings of the two images of the line is D , and the number of divisions of the scale of sliding tube at which the telescope was focussed was a . To determine whether the angle so found was to be added or subtracted from the reading of the circle, all that was necessary was to observe whether the micrometer reading of the upper or lower image as seen in the microscope were the greater. The angular position of the line having thus been found on each side of the collimator, the wave-length was deduced by the ordinary formula.

The following tables give the measurements made, the calculated angles, and the wave-lengths deduced.

The quantities recorded in the several columns are as follows:—

- I. The mark of the particular photographic plate.
- II. The reading of the circle, giving the position of the telescope.
- III. The reading of the scale of focussing tube.
- IV. The measured distance of the two images of the line in hundredths of an inch.
- V. One half this distance reduced to angular measure with the sign + or — according as it is to be added or subtracted from the reading of the circle to give the angular position of the line.
- VI. The angular position of the line.
- VII. The mean values of the angular positions so found. When several sets of plates have been taken at different times, or with varied adjustments, the means for the several sets are given separately.

VIII. The deviation from the normal to the grating of the line as deduced.

IX. The wave-length deduced or adopted. When different sets of plates give different values, these different values are inserted in brackets.

The figures belonging to different lines are separated by horizontal spaces.

In the case of plates marked with a figure less than 172 the arc was employed to give the light, in the case of all plates with the mark 172 and upwards the spark was employed.

I	II			III	IV	V		VI			VII			VIII			IX
	°	'	"		hundredths of an inch	'	"	°	'	"	°	'	"	°	'	"	wave- length
341	28	30	0	49	10·63	-11	12	28	18	48							
342	309	30	0	49	8·43	+ 8	53	309	38	53							
343	309	25	0	49	13·39	+14	6	309	39	6	309	39	0	39	19	54	2326·9
341	28	30	0	49	6·11	- 6	26	28	23	34							
342	309	30	0	49	3·96	+ 4	10	309	34	10							
343	309	25	0	49	8·72	+ 9	11	309	34	11				39	24	42	2330·9
341	28	30	0	49	4·36	- 4	35	28	25	25							
342	309	30	0	49	2·01	+ 2	7	309	32	7							
343	309	25	0	49	6·92	+ 7	17	309	32	17	309	32	12	39	26	36	2332·5
341	28	30	0	49	1·64	+ 1	44	28	31	44							
342	309	30	0	49	3·96	- 4	10	309	25	50							
343	309	25	0	49	0·87	+ 0	55	309	25	55	309	25	52	39	32	56	2337·7
341	28	30	0	49	7·92	+ 8	20	28	38	20							
342	309	30	0	49	10·37	-10	55	309	19	5							
343	309	25	0	49	5·57	- 5	52	309	19	8	309	19	6	39	39	37	2343·2
341	28	30	0	49	8·78	+ 9	15	28	39	15							
342	309	30	0	49	11·27	-11	52	309	18	8							
343	309	25	0	49	6·36	- 6	42	309	18	18	309	18	13	39	40	31	2343·9
341	28	30	0	49	13·40	+14	7	28	44	7							
342	309	30	0	49	15·89	-16	44	309	13	16							
343	309	25	0	49	11·07	-11	39	309	13	21	309	13	14	39	45	27	2348·0
262	28	45	0	50	11·67	+12	16	28	57	16							
263	28	40	0	50	16·38	+17	14	28	57	14	28	57	15				
264	309	15	0	50	13·97	-14	42	309	0	18							
265	309	10	0	50	9·18	- 9	39	309	0	21	309	0	19	39	58	28	2358·7
262	28	45	0	50	12·91	+13	35	28	58	35							
263	28	40	0	50	17·63	+18	33	28	58	33	28	58	34				
264	309	15	0	50	15·15	-15	56	308	59	4							
265	309	10	0	50	10·44	-10	59	308	59	1	308	59	2	39	59	46	2359·7
262	28	45	0	50	18·33	+19	17	29	4	17							
263	28	40	0	50	23·02	+24	13	29	4	13	29	4	15				
264	309	15	0	50	20·68	-21	45	308	53	15							
265	309	10	0	50	15·98	-16	48	308	53	12	308	53	13	40	5	31	2364·4

I	II	III	IV	V	VI	VII	VIII	IX
	° ' "		hundredths of an inch	' "	° ' "	° ' "	° ' "	wave- length
81	29 30 3	25	1.70	+ 1 51	29 31 54			
82	29 30 3	25	2.02	+ 2 12	29 32 15			
86	29 34 3	25	2.37	- 2 35	29 31 28	29 31 52		
84	308 59 40	25	1.52	- 1 39	308 58 1			
85	308 59 40	25	1.20	- 1 18	308 58 22	308 58 12	40 16 50	(2373.7)
100	308 53 50	25	2.47	- 2 41	308 51 9			
101	308 53 50	25	2.66	- 2 53	308 50 57	308 51 3		
102	29 40 0	25	14.64	-15 53	29 24 7			
103	29 30 0	25	5.40	- 5 52	29 24 8	29 24 7	40 16 32	2373.4
262	28 45 0	50	28.65	+30 8	29 15 8			
263	28 40 0	50	33.33	+35 3	29 15 3	29 15 6		
264	309 15 0	50	31.09	-32 42	308 42 18			
265	309 10 0	50	26.36	-27 43	308 42 17	308 42 17	40 16 25	(2373.3)
262	28 45 0	50	38.19	+40 10	29 25 10			
263	28 40 0	50	42.96	+45 11	29 25 11	29 25 11		
264	309 15 0	50	40.87	-42 59	308 32 1			
265	309 10 0	50	36.11	-37 59	308 32 1		40 26 35	(2381.6)
81	29 30 3	25	11.29	+12 14	29 42 17			
82	29 30 3	25	11.62	+12 36	29 42 39			
86	29 34 3	25	7.13	+ 7 44	29 41 47	29 42 14		
84	308 59 40	25	11.02	-11 57	308 47 43			
85	308 59 40	25	10.82	-11 44	308 47 56	308 47 48	40 27 13	(2382.1)
100	308 53 50	25	12.00	-13 1	308 40 49			
101	308 53 50	25	12.26	-13 18	308 40 32	308 40 40		2381.7
102	29 40 0	25	5.27	- 5 43	29 34 17			
103	29 30 0	25	4.10	+ 4 27	29 34 27	29 34 22	40 26 51	(2381.8)
258	308 15 0	53	16.34	+17 7	308 32 7			
259	308 20 0	53	11.86	+12 26	308 32 26	308 32 17		
260	29 45 0	53	18.78	-19 41	29 25 19			
261	29 40 0	53	13.70	-14 21	29 25 39	29 25 29	40 26 36	(2381.6)
81	29 30 3	25	18.96	+20 34	29 50 37			
82	29 30 3	25	19.14	+20 55	29 50 58			
86	29 34 3	25	14.66	+15 54	29 49 57	29 50 31		
84	308 59 40	25	18.66	-20 15	308 39 25			
85	308 59 40	25	18.45	-20 1	308 39 39	308 39 32	40 35 29	(2388.8)
258	308 15 0	53	8.56	+ 8 58	308 23 58			
259	308 20 0	53	4.01	+ 4 12	308 24 12	308 24 5		
260	29 45 0	53	11.02	-11 33	29 33 27			
261	29 40 0	53	5.89	- 6 10	29 33 50	29 33 38	40 34 46	(2388.2)
100	308 53 50	25	19.61	-21 17	308 32 33			
101	308 53 50	25	19.77	-21 27	308 32 23	308 32 28		
102	29 40 0	25	2.31	+ 2 30	29 42 30			
103	29 30 0	25	11.64	+12 38	29 42 38	29 42 34	40 35 3	2388.5
100	308 53 50	25	27.60	-29 57	308 23 53			
101	308 53 50	25	27.79	-30 9	308 23 4	308 23 47		
102	29 40 0	25	10.33	+11 12	29 51 12			
103	29 30 0	25	19.64	+21 18	29 51 18	29 51 15	40 43 44	(2395.5)

I	II	III	IV	V	VI	VII	VIII	IX
	° ' "		hundredths of an inch	' "	° ' "	° ' "	° ' "	wave- length
258	308 15 0	53	0·22	+ 0 14	308 15 14			
259	308 20 0	53	4·41	- 4 37	308 15 23	308 15 18		2395·4
260	29 45 0	53	2·85	- 3 3	29 41 57			
261	29 40 0	53	2·20	+ 2 18	29 42 18	29 42 7	40 43 24	(2395·2)
100	308 53 50	25	31·80	-34 30	308 19 20			
101	308 53 50	25	32·03	-34 45	308 19 5	308 19 12		
102	29 40 0	25	14·46	+15 41	29 55 41			
103	29 30 0	25	23·85	+25 53	29 55 53	29 55 47	40 48 18	(2399·2)
258	308 15 0	53	4·16	- 4 22	308 10 38			
259	308 20 0	53	8·65	- 9 4	308 10 56	308 10 47		2399
260	29 45 0	53	1·45	+ 1 31	29 46 31			
261	29 40 0	53	6·53	+ 6 51	29 46 51	29 46 41	40 47 57	(2398·9)
258	308 15 0	53	10·89	-11 25	308 3 35			
259	308 20 0	53	15·48	-16 13	308 3 47	308 3 41		
260	29 45 0	53	8·08	+ 8 28	29 53 28			
261	29 40 0	53	13·13	+13 46	29 53 46	29 53 37	40 54 58	2404·5
258	308 15 0	53	12·97	-13 36	308 1 24			
259	308 20 0	53	17·53	-18 22	308 1 38	308 1 31		
260	29 45 0	53	10·18	+10 40	29 55 40			
261	29 40 0	53	15·18	+15 54	29 55 54	29 55 47	40 57 8	2406·3
258	308 15 0	53	17·57	-18 25	307 56 35			
259	308 20 0	53	22·12	-23 11	307 56 49	307 56 42		
260	29 45 0	53	14·65	+15 21	30 0 21			
261	29 40 0	53	19·69	+20 38	30 0 38	30 0 30	41 1 54	2410·2
258	308 15 0	53	18·20	-19 4	307 55 56			
259	308 20 0	53	22·79	-23 53	307 56 7	307 56 1		
260	29 45 0	53	15·41	+16 9	30 1 9			
261	29 40 0	53	20·35	+21 20	30 1 20	30 1 15	41 2 37	2410·7
258	308 15 0	53	20·93	-21 56	307 53 4			
259	308 20 0	53	25·55	-26 46	307 53 14	307 53 9		
260	29 45 0	53	17·99	+18 51	30 3 51			
261	29 40 0	53	23·01	+24 7	30 4 7	30 3 59	41 5 25	2413·0
254	30 45 0	57	7·82	- 8 9	30 36 51			
255	30 40 0	57	3·05	- 3 11	30 36 49	30 36 50		
256	307 15 0	57	5·71	+ 5 57	307 20 57			
257	307 20 0	57	1·06	+ 1 6	307 21 6	307 21 2	41 37 54	2439·0
254	30 45 0	57	1·60	- 1 40	30 43 20			
255	30 40 0	57	3·17	+ 3 18	30 43 18	30 43 19		
256	307 15 0	57	0·67	- 0 42	307 14 18			
257	307 20 0	57	5·37	- 5 36	307 14 24	307 14 21	41 44 29	2444·3
254	30 45 0	57	0·27	- 0 17	30 44 43			
255	30 40 0	57	4·45	+ 4 38	30 44 38	30 44 41		
256	307 15 0	57	1·98	- 2 4	307 12 56			
257	307 20 0	57	6·70	- 6 59	307 13 1	307 12 58	41 45 52	2445·4
250	32 0 0	65	47·16	-48 42	31 11 18			
251	306 5 0	65	40·20	+41 31	306 46 31		42 12 23	2466·4

I	II			III	IV	V	VI	VII	VIII	IX				
	°	'	"		hundredths of an inch	'	"	°	'	"	°	'	"	wave- length
250	32	0	0	65	42.39	-43	47	31	16	13				
251	306	5	0	65	35.41	+36	34	306	41	34			42 17 19	2470.3
250	32	0	0	65	30.79	-31	48	31	28	12				
253	31	45	0	65	16.06	-16	35	31	28	25	31	28	18	
251	306	5	0	65	23.53	+24	18	306	29	18				
252	306	15	0	65	13.80	+14	15	306	29	15	306	29	17	42 29 31 2480.0
250	32	0	0	65	28.43	-29	22	31	30	38				
253	31	45	0	65	13.78	-14	14	31	30	46	31	30	42	
251	306	5	0	65	21.27	+21	58	306	26	58				
252	306	15	0	65	11.42	+11	48	306	26	48	306	26	53	42 31 54 2481.8
250	32	0	0	65	27.73	-28	38	31	31	22				
251	306	5	0	65	20.52	+21	12	306	26	12			42 32 35	2482.4
71	31	54	45	50	3.07	- 3	14	31	51	31				
72	306	38	55	50	5.78	+ 6	5	306	45	0				
73	306	38	55	50	5.79	+ 6	5	306	45	0	306	45	0	42 33 15 2482.9
71	31	54	45	50	2.04	- 2	9	31	52	36				
72	306	38	55	50	4.77	+ 5	1	306	43	56				
73	306	38	55	50	4.85	+ 5	6	306	44	1	306	43	59	42 34 18 2483.7
250	32	0	0	65	23.27	-24	2	31	35	58				
253	31	45	0	65	8.35	- 8	37	31	36	23	31	36	10	
251	306	5	0	65	16.24	+16	46	306	21	46				
252	306	15	0	65	6.02	+ 6	13	306	21	13	306	21	30	42 37 20 2486.1
107	306	10	10	50	17.40	+18	18	306	28	28				
108	306	0	0	50	27.46	+28	53	306	28	53				
109	306	10	10	50	17.71	+18	36	306	28	46				
110	306	20	0	50	8.64	+ 9	6	306	29	6	306	28	48	
111	32	0	5	50	11.83	-12	27	31	47	33				
112	32	0	5	50	12.02	-12	39	31	47	26	31	47	33	42 39 23 2487.7
113	31	50	10	50	2.39	- 2	31	31	47	39				
71	31	54	45	50	4.74	+ 4	59	31	59	44				
72	306	38	55	50	2.06	- 2	10	306	36	45				
73	306	38	55	50	2.08	- 2	11	306	36	44	306	36	44	42 41 30 (2489.4)
172	31	50	5	50	2.00	- 2	6	31	47	59				
173	31	40	20	50	7.41	+ 7	48	31	48	8				
174	32	0	5	50	11.67	-12	16	31	47	49	31	47	59	
175	306	23	0	50	1.04	+ 1	6	306	24	6				2489.5
176	306	33	5	50	8.37	- 8	48	306	24	17				
177	306	13	0	50	10.74	+11	18	306	24	18	306	24	14	42 41 53 (2489.7)
250	32	0	0	65	19.12	-19	45	31	40	15				
253	31	45	0	65	4.34	- 4	29	31	40	31	31	40	23	
251	306	5	0	65	11.64	+12	1	306	17	1				
252	306	15	0	65	1.79	+ 1	54	306	16	54	306	16	57	42 41 43 2489.5
250	32	0	0	65	17.91	-18	30	31	41	30				
253	31	45	0	65	3.12	- 3	13	31	41	47	31	41	38	
251	306	5	0	65	10.51	+10	51	306	15	51				
252	306	15	0	65	0.73	+ 0	45	306	15	45	306	15	48	42 42 55 2490.5

I	II			III	IV	V	VI	VII	VIII	IX				
	°	'	"		hundredths of an inch	'	"	°	'	"	°	'	"	wave- length
250	32	0	0	65	14.87	- 15	21	31	44	39				
253	31	45	0	65	0.09	- 0	6	31	44	54	31	44	46	
251	306	5	0	65	7.42	+ 7	40	306	12	40				
252	306	15	0	65	2.41	- 2	29	306	12	29	306	12	35	2493.0
172	31	50	5	50	2.19	+ 2	18	31	52	23				
173	31	40	20	50	11.59	+12	11	31	52	31				
174	32	0	5	50	7.55	- 7	56	31	52	9	31	52	21	
175	306	23	0	50	3.19	- 3	22	306	19	38				2493.0
176	306	33	5	50	12.59	-13	15	306	19	50				
177	306	13	0	50	6.53	+ 6	52	306	19	52	306	19	47	(2493.1)
246*	305	20	0	65	51.22	+52	54	306	12	54				
247	305	25	0	65	46.37	+47	53	306	12	53	306	12	54	
248	32	45	0	65	58.23	-60	8	31	44	52				
249	32	40	0	65	53.28	-55	1	31	44	59	31	44	55	(2492.9)
246*	305	20	0	65	44.18	+45	38	306	5	38				
247	305	25	0	65	39.34	+40	38	306	5	38				
248	32	45	0	65	51.14	-52	49	31	52	11				
249	32	40	0	65	46.31	-47	50	31	52	11				
172	31	50	5	50	8.97	+ 9	26	31	59	31				
173	31	40	20	50	18.45	+19	24	31	59	44				
174	32	0	5	50	0.64	- 0	40	31	59	25	31	59	33	
175	306	23	0	50	10.13	-10	39	306	12	21				2498.7
176	306	33	5	50	19.56	-20	34	306	12	31				
177	306	13	0	50	0.42	- 0	27	306	12	33	306	12	30	(2498.8)
91	306	39	0	50	26.86	-28	15	306	10	45				
92	31	55	0	50	24.04	+25	17	32	20	17				
93	31	55	0	50	23.92	+25	10	32	20	10	32	20	14	2507.6
181	305	22	0	55	33.07	+34	34	305	56	34	305	56	34	
182	32	56	10	55	38.61	-40	22	32	15	48				
183	32	55	5	55	37.47	-39	10	32	15	55				
184	32	51	15	55	33.88	-35	25	32	15	50				
185	32	35	2	55	18.40	-19	14	32	15	48				
186	32	25	15	55	9.02	- 9	26	32	15	49	32	15	50	2511.4
246*	305	20	0	65	28.14	+29	4	305	49	4				
247	305	25	0	65	23.20	+23	54	305	48	54	305	48	59	
248	32	45	0	65	35.35	-36	31	32	8	29				
249	32	40	0	65	30.54	-31	33	32	8	27	32	8	28	2511.4
246*	305	20	0	65	10.95	+11	19	305	31	19				
247	305	25	0	65	5.97	+ 6	10	305	31	10	305	31	15	
248	32	45	0	65	18.43	-19	2	32	25	58				
249	32	40	0	65	13.56	-14	0	32	26	0	32	25	59	(2525.2)
181	305	22	0	55	16.10	+16	50	305	38	50	305	38	50	
182	32	56	10	55	22.02	-23	1	32	33	9				
183	32	55	5	55	20.82	-21	46	32	33	19				
184	32	51	15	55	17.24	-18	1	32	33	14				
185	32	35	2	55	1.72	- 1	48	32	33	14				
186	32	25	15	55	7.69	+ 8	2	32	33	17	32	33	15	2525.1

I	II	III	IV	V	VI	VII	VIII	IX
	° ' "		hundredths of an inch	' "	° ' "	° ' "	° ' "	wave- length
246*	305 20 0	65	9·81	+10 8	305 30 8			
247	305 25 0	65	4·84	+ 5 0	305 30 0	305 30 4		
248	32 45 0	65	17·35	-17 55	32 27 5			
249	32 40 0	65	12·48	-12 53	32 27 7	32 27 6	43 28 31	2526·1
246*	305 20 0	65	5·72	+ 5 54	305 25 54			
247	305 25 0	65	0·78	+ 0 48	305 25 48	305 25 51		
248	32 45 0	65	13·25	-13 41	32 31 19			
249	32 40 0	65	8·32	- 8 36	32 31 24	32 31 22	43 32 45	(2529·3)
178	305 53 10	55	19·06	-19 55	305 33 15			
179	305 47 55	55	13·90	-14 32	305 33 23			
180	305 18 0	55	14·84	+15 31	305 33 31			
181	305 22 0	55	10·92	+11 25	305 33 25	305 33 23		
182	32 56 10	55	16·92	-17 42	32 38 28			
183	32 55 5	55	15·70	-16 25	32 38 40			
184	32 51 15	55	12·23	-12 47	32 38 28			
185	32 35 2	55	3·42	+ 3 35	32 38 37			
186	32 25 15	55	12·87	+13 27	32 38 42	32 38 35	43 32 36	2529·2
246*	305 20 0	65	0·55	+ 0 34	305 20 34			
247	305 25 0	65	4·39	- 4 32	305 20 28	305 20 31		
248	32 45 0	65	8·22	- 8 29	32 36 31			
249	32 40 0	65	3·27	- 3 23	32 36 37	32 36 34	43 38 2	2533·4
246*	305 20 0	65	0·35	- 0 22	305 19 38			
247	305 25 0	65	5·31	- 5 29	305 19 29	305 19 34		
248	32 45 0	65	7·20	- 7 26	32 37 34			
249	32 40 0	65	2·32	- 2 24	32 37 36	32 37 35	43 39 0	2534·2
246*	305 20 0	65	3·41	- 3 31	305 16 29			
247	305 25 0	65	8·27	- 8 33	305 16 27	305 16 28		
248	32 45 0	65	4·24	- 4 23	32 40 37			
249	32 40 0	65	0·65	+ 0 40	32 40 40	32 40 38	43 42 5	2536·6
178	305 53 10	55	28·22	-29 30	305 23 40			
179	305 47 55	55	23·04	-24 5	305 23 50			
180	305 18 0	55	5·71	+ 5 58	305 23 58			
181	305 22 0	55	1·74	+ 1 52	305 23 52	305 23 50		
182	32 56 10	55	7·90	- 8 15	32 47 55			
183	32 55 5	55	6·67	- 6 58	32 48 7			
184	32 51 15	55	3·20	- 3 21	32 47 54			
185	32 35 2	55	12·36	+12 55	32 47 57			
186	32 25 15	55	21·79	+22 47	32 48 2	32 47 59	43 42 5	2536·6
178	305 53 10	55	30·92	-32 19	305 20 51			
179	305 47 55	55	25·71	-26 53	305 21 2			
180	305 18 0	55	3·11	+ 3 15	305 21 15			
181	305 22 0	55	0·91	- 0 57	305 21 3	305 21 3		
182	32 56 10	55	5·40	- 5 39	32 50 31			
183	32 55 5	55	4·13	- 4 19	32 50 46			
184	32 51 15	55	0·76	- 0 48	32 50 27			
185	32 35 2	55	14·95	+15 38	32 50 40			
186	32 25 15	55	24·30	+25 24	32 50 39	32 50 37	43 44 47	2538·6
187	33 10 10	62	18·64	-19 19	32 50 51			
188	33 20 15	62	28·24	-29 16	32 50 59	32 50 55		
189	305 3 0	62	17·86	+18 31	305 21 31			
190	304 52 40	62	27·59	+28 36	305 21 16	305 21 23	43 44 46	2538·6

I	II	III	IV	V	VI	VII	VIII	IX
			hundredths of an inch					wave- length
243	° 33 25 0	65	40·47	-41 48	° 32 43 12	° ' "	° ' "	
244	33 15 0	65	30·78	-31 47	32 43 13			
248	32 45 0	65	1·61	- 1 40	32 43 20			
249	32 40 0	65	3·27	+ 3 23	32 43 23	32 43 17		
245	304 50 0	65	23·15	+23 55	305 13 55			
246	304 45 0	65	27·85	+28 46	305 13 46			
246*	305 20 0	65	6·01	- 6 12	305 13 48			
247	305 25 0	65	11·01	-11 22	305 13 38	305 13 47	43 44 45	2538·6
242	33 30 0	65	32·13	-33 11	32 56 49			
243	33 25 0	65	27·25	-28 9	32 56 51			
244	33 15 0	65	17·63	-18 13	32 56 47	32 56 49		
245	304 50 0	65	9·83	+10 9	305 0 9			
246	304 45 0	65	14·56	+15 2	305 0 2	305 0 6	43 58 21	2549·1
242	33 30 0	65	31·41	-32 26	32 57 34			
243	33 25 0	65	26·58	-27 27	32 57 33			
244	33 15 0	65	16·87	-17 26	32 57 34	32 57 34		
245	304 50 0	65	8·99	+ 9 17	304 59 17			
246	304 45 0	65	13·77	+14 13	304 59 13	304 59 15	43 59 10	2549·7
242	33 30 0	65	30·64	-31 39	32 58 21			
243	33 25 0	65	25·75	-26 36	32 58 24			
244	33 15 0	65	16·12	-16 39	32 58 21	32 58 22		
245	304 50 0	65	8·19	+ 8 28	304 58 28			
246	304 45 0	65	12·89	+13 19	304 58 19	304 58 23	43 59 59	2550·3
242	33 30 0	65	15·64	-16 9	33 13 51			
243	33 25 0	65	10·74	-11 6	33 13 54			
244	33 15 0	65	1·13	- 1 10	33 13 50	33 13 52		
245	304 50 0	65	6·97	- 7 12	304 42 48			
246	304 45 0	65	2·27	- 2 21	304 42 39	304 42 43	44 15 34	2562·3
188	33 20 15	62	1·31	+ 1 21	33 21 36	33 21 36		
189	305 3 0	62	11·86	-12 18	304 50 42			
190	304 52 40	62	2·25	- 2 20	304 50 20	304 50 31	44 15 33	2562·3
242	33 30 0	65	14·50	-14 59	33 15 1			
243	33 25 0	65	9·57	- 9 53	33 15 7			
244	33 15 0	65	0·10	+ 0 6	33 15 6	33 15 5		
245	304 50 0	65	7·96	- 8 13	304 41 47			
246	304 45 0	65	3·45	- 3 34	304 41 26	304 41 36	44 16 44	2563·2
193	303 19 55	57	57·80	+60 16	304 20 11			
194	34 53 15	57	58·93	-61 27	33 51 48		44 45 48	(2585·3)
195	34 43 5	54	49·10	-51 23	33 51 42			
196	303 30 0	54	47·72	+49 57	304 9 57		44 45 52	2585·4
242	33 30 0	65	13·75	+14 12	33 44 12			
243	33 25 0	65	18·57	+19 11	33 44 11			
244	33 15 0	65	28·30	+29 14	33 44 14	33 44 12		
245	304 50 0	65	36·59	-37 47	304 12 13			
246	304 45 0	65	32·00	-33 3	304 11 57	304 12 5	44 46 4	(2585·5)
96	303 19 57	65	45·14	+46 37	304 6 34			
97	303 19 57	65	44·91	+46 26	304 6 23	304 6 29		
98	34 50 0	65	38·13	-39 23	34 10 37			
99	34 50 0	65	37·99	-39 14	34 10 46	34 10 41	45 2 6	2597·6

I	II	III	IV	V	VI	VII	VIII	IX
	° ' "		hundredths of an inch	' "	° ' "	° ' "	° ' "	wave- length
96	303 19 57	65	43·80	+45 14	304 5 11			
97	303 19 57	65	43·63	+45 4	304 5 1	304 5 6		
98	34 50 0	65	36·71	-37 55	34 12 5			
99	34 50 0	65	36·49	-37 41	34 12 19	34 12 12	45 3 33	(2598·7)
195	34 43 5	54	32·03	-33 32	34 9 33			
196	303 30 0	54	30·34	+31 45	304 1 45		45 3 54	(2599·0)
193	303 19 55	57	40·38	+42 2	304 1 58			2598·8
194	34 53 15	57	41·75	-43 32	34 9 43		45 3 52	(2599·0)
195	34 43 5	54	22·35	-23 24	34 19 41			
196	303 30 0	54	20·59	+21 33	303 51 33		45 14 4	(2606·6)
193	303 19 55	57	30·45	+31 45	303 51 40			2606·7
194	34 53 15	57	31·77	-33 8	34 20 7		45 14 13	(2606·8)
193	303 19 55	57	24·28	+25 19	303 45 14			
194	34 53 15	57	25·84	-26 57	34 26 18		45 20 32	(2611·5)
195	34 43 5	54	16·24	-17 0	34 26 5			
196	303 30 0	54	11·57	+15 15	303 45 15		45 20 25	2611·4
96	303 19 57	65	27·72	+28 38	303 48 35			
97	303 19 57	65	27·54	+28 27	303 48 24	303 48 30		
98	34 50 0	65	20·89	-21 34	34 28 26			
99	34 50 0	65	20·75	-21 26	34 28 34	34 28 30	45 20 0	(2611·1)
96	303 19 57	65	25·14	+25 58	303 45 55			
97	303 19 57	65	24·93	+25 45	303 45 42	303 45 49		
98	34 50 0	65	18·34	-18 57	34 31 3			
99	34 50 0	65	18·33	-18 56	34 31 4	34 31 3	45 22 37	2613·1
96	303 19 57	65	20·18	+20 50	303 40 47			
97	303 19 57	65	20·05	+20 42	303 40 39	303 40 43		
98	34 50 0	65	13·41	-13 51	34 36 9			
99	34 50 0	65	13·28	-13 43	34 36 17	34 36 13	45 27 45	(2616·9)
195	34 43 5	54	8·94	- 9 21	34 33 44			
196	303 30 0	54	7·18	+ 7 31	303 37 31		45 28 6	2617·2
193	303 19 55	57	16·92	+17 39	303 37 33			
194	34 53 15	57	18·54	-19 20	34 33 55		45 28 11	2617·2
193	303 19 55	57	6·58	+ 6 52	303 26 47			
194	34 53 15	57	8·29	- 8 39	34 44 36		45 38 55	(2625·3)
195	34 43 5	54	1·18	+ 1 14	34 44 19			
196	303 30 0	54	3·14	- 3 17	303 26 43		45 38 48	2625·2
96	303 19 57	65	9·76	+10 5	303 30 2			
97	303 19 57	65	9·45	+ 9 46	303 29 43	303 29 53		
98	34 50 0	65	2·96	- 3 4	34 46 56			
99	34 50 0	65	2·84	- 2 55	34 47 5	34 47 0	45 38 33	(2625·0)
237	34 30 0	73	7·12	+ 7 17	34 37 17			
238	34 25 0	73	11·88	+12 9	34 37 9	34 37 11		
239	303 0 0	70	18·88	+19 19	303 19 19	303 19 18	45 38 56	(2625·3)
240	303 15 0	70	4·18	+ 4 17	303 19 17			
241	34 45 0	70	7·68	- 7 53	34 37 7			

I	II	III	IV	V	VI	VII	VIII	IX
			hundredths of an inch					wave- length
96	303 19 57	65	6.18	+ 6 23	303 26 20			
97	303 19 57	65	5.91	+ 6 6	303 26 3	303 26 12		
98	34 50 0	65	0.52	+ 0 32	34 50 32			
99	34 50 0	65	0.63	+ 0 39	34 50 39	34 50 35	45 42 12	(2627.7)
193	303 19 55	57	3.12	+ 3 20	303 23 15			
194	34 53 15	57	4.94	- 5 9	34 48 6		45 42 25	2627.9
237	34 30 0	73	10.63	+ 10 53	34 40 53			
238	34 25 0	73	15.41	+ 15 46	34 40 46	34 40 47		
239	303 0 0	70	15.44	+ 15 48	303 15 48	303 15 45	45 42 31	2627.9
240	303 15 0	70	0.66	+ 0 41	303 15 41			
241	34 45 0	70	4.16	- 4 16	34 40 44			
195	34 43 5	54	4.62	+ 4 51	34 47 56			
196	303 30 0	54	6.53	- 6 50	303 23 10		45 42 23	2627.9
96	303 19 57	65	2.49	+ 2 34	303 22 31			
97	303 19 57	65	2.23	+ 2 18	303 22 15	303 22 23		
98	34 50 0	65	4.34	+ 4 29	34 54 29			
99	34 50 0	65	4.45	+ 4 36	34 54 36	34 54 33	45 46 5	(2630.6)
193	303 19 55	57	0.61	- 0 38	303 19 17			
194	34 53 15	57	1.41	- 1 28	34 51 47		45 46 15	2630.7
195	34 43 5	54	8.15	+ 8 32	34 51 37			
196	303 30 0	54	10.07	- 10 32	303 19 28		45 46 5	(2630.6)
237	34 30 0	73	14.27	+ 14 36	34 44 36			
238	34 25 0	73	18.99	+ 19 26	34 44 26	34 44 29		
239	303 0 0	70	11.58	+ 11 51	303 11 51	303 11 55	45 46 17	(2630.8)
240	303 15 0	70	2.93	- 3 1	303 11 59			
241	34 45 0	70	0.59	- 0 36	34 44 24			
195	34 43 5	54	51.32	+ 53 36	35 36 41			
196	303 30 0	54	53.71	- 56 13	302 33 47		46 31 27	(2664.2)
232	302 30 0	76	2.77	- 2 49	302 27 11			
234	302 35 0	76	7.66	- 7 48	302 27 12	302 27 11		
235	35 30 0	76	0.16	- 0 10	35 29 50		46 31 20	2664.1
323	302 25 0	76	2.84	+ 2 54	302 27 54			
324	35 30 0	76	0.00	0 0	35 30 0		46 31 3	(2663.9)
195	34 43 5	54	53.96	+ 56 28	35 39 33			
196	303 30 0	54	56.38	- 59 0	302 31 0		46 34 17	(2666.3)
323	302 25 0	76	0.23	+ 0 14	302 25 14			
324	35 30 0	76	2.57	+ 2 37	35 32 37		46 33 42	(2665.8)
232	302 30 0	76	5.41	- 5 31	302 24 29			
234	302 35 0	76	10.32	- 10 31	302 24 29	302 24 29		
235	35 30 0	76	2.51	+ 2 34	35 32 34		46 34 3	2666.1
225	37 0 0	79	61.41	- 62 22	35 57 38			
228	36 30 0	79	32.14	- 32 39	35 57 21	35 57 29		
226	301 5 0	79	53.53	+ 54 22	301 59 22			
227	301 35 0	79	24.15	+ 24 32	301 59 32	301 59 27	46 59 1	(2684.4)

I	II	III	IV	V	VI	VII	VIII	IX
	° ' "		hundredths of an inch	' "	° ' "	° ' "	° ' "	wave- length
232	302 30 0	76	29·89	-30 28	301 59 32			
234	302 35 0	76	34·72	-35 23	301 59 37	301 59 34		2684·2
235	35 30 0	76	26·71	+27 14	35 57 14			
236	35 35 0	76	21·87	+22 18	35 57 18	35 57 16	46 58 51	(2684·3)
323	302 25 0	76	24·21	-24 41	302 0 19			
324	35 30 0	76	26·82	+27 21	35 57 21		46 58 31	(2684·0)
232	302 30 0	76	40·61	-41 24	301 48 36			
234	302 35 0	76	45·34	-46 12	301 48 48	301 48 42		
235	35 30 0	76	37·31	+38 2	36 8 2			
236	35 35 0	76	32·46	+33 5	36 8 5	36 8 4	47 9 41	2692·1
323	302 25 0	76	34·83	-35 30	301 49 30			
324	35 30 0	76	37·46	+38 11	36 8 11		47 9 21	(2691·9)
225	37 0 0	79	50·81	-51 36	36 8 24			
228	36 30 0	79	21·49	-21 50	36 8 10	36 8 17		2692·1
226	301 5 0	79	42·77	+43 26	301 48 26			
227	301 35 0	79	13·40	+13 37	301 48 37	301 48 32	47 9 52	(2692·2)
225	37 0 0	79	35·43	-35 59	36 24 1			
228	36 30 0	79	6·09	-6 11	36 23 49	36 23 55		
226	301 5 0	79	27·19	+27 37	301 32 37			
227	301 35 0	79	2·23	-2 16	301 32 44	301 32 41	47 25 37	2703·6
197	300 59 55	65	25·63	+26 28	301 26 23			
198	301 10 0	65	15·74	+16 16	301 26 16	301 26 20		
200	37 3 0	65	16·83	-17 23	36 45 37			
201	37 12 55	65	26·64	-27 31	36 45 24	36 45 30	47 39 35	(2713·7)
225	37 0 0	79	21·26	-21 36	36 38 24			
228	36 30 0	79	8·10	+8 14	36 38 14	36 38 19		2713·8
226	301 5 0	79	12·95	+13 9	301 18 9			
227	301 35 0	79	16·48	-16 21	301 18 39	301 18 24	47 39 58	(2714·0)
225	37 0 0	79	3·43	-3 29	36 56 31			
228	36 30 0	79	26·04	+26 27	36 56 27	36 56 29		
226	301 5 0	79	5·05	-5 8	300 59 52			
227	301 35 0	79	34·46	-35 0	301 0 0	300 59 56	47 58 16	(2727·1)
197	300 59 55	65	7·78	+8 2	301 7 57			
198	301 10 0	65	2·14	-2 13	301 7 57	301 7 57		2727·0
200	37 3 0	65	0·88	+0 55	37 3 55			
201	37 12 55	65	8·75	-9 2	37 3 53	37 3 54	47 57 58	(2726·9)
197	300 59 55	65	8·68	-8 58	300 50 57			
198	301 10 0	65	18·58	-19 11	300 50 49	300 50 55		
200	37 3 0	65	17·27	+17 50	37 20 50			
201	37 12 55	65	7·59	+7 50	37 20 45	37 20 48	48 14 57	(2739·0)
229	37 30 0	86	16·07	-16 11	37 13 49			2739·1
230	300 35 0	86	7·97	+8 2	300 43 2			
231	300 30 0	86	12·87	+12 58	300 42 58	300 43 0	48 15 24	(2739·3)
229	37 30 0	86	10·99	-11 4	37 18 56			
230	300 35 0	86	2·88	+2 54	300 37 54			
231	300 30 0	86	7·81	+7 52	300 37 52	300 37 53	48 20 31	(2743·0)

I	II			III	IV	V	VI	VII	VIII	IX						
	°	'	"		hundredths of an inch	'	"	°	'	"	°	'	"			wave- length
197	300	59	55	65	13·79	- 14	15	300	45	40						
198	301	10	0	65	23·62	- 24	24	300	45	36	300	45	38			2742·8
200	37	3	0	65	22·23	+ 22	57	37	25	57						
201	37	12	55	65	12·47	+ 12	53	37	25	48	37	25	53	48	20	8 (2742·7)
197	300	59	55	65	18·35	- 18	57	300	40	58						
198	301	10	0	65	28·21	- 29	18	300	40	52	300	40	55			(2746·0)
200	37	3	0	65	26·68	+ 27	33	37	30	33						
201	37	12	55	65	17·04	+ 17	36	37	30	31	37	30	32	48	24	49 2746·1
229	37	30	0	86	6·46	- 6	31	27	23	29						
230	300	35	0	86	1·71	- 1	43	300	33	17						
231	300	30	0	86	3·27	+ 3	18	300	33	18	300	33	17	48	25	6 (2746·2)
229	37	30	0	86	5·78	- 5	49	37	24	11						
230	300	35	0	86	2·38	- 2	24	300	32	36						
231	300	30	0	86	2·56	+ 2	35	300	32	35	300	32	36	48	25	47 2746·7
197	300	59	55	65	18·99	- 19	37	300	40	18						
198	301	10	0	65	28·85	- 29	48	300	40	12	300	40	15			
200	37	3	0	65	27·38	+ 28	17	37	31	17						
201	37	12	55	65	17·69	+ 18	39	37	31	34	37	31	26	48	25	36 (2746·6)
197	300	59	55	65	22·23	- 22	58	300	36	57						
198	301	10	0	65	32·12	- 33	10	300	36	50	300	36	53			
200	37	3	0	65	30·57	+ 31	34	37	34	34						
201	37	12	55	65	20·97	+ 22	7	37	35	2	37	34	48	48	28	58 (2749·1)
229	37	30	0	86	2·51	- 2	32	37	27	28						
230	300	35	0	86	5·65	- 5	41	300	29	19						
231	300	30	0	86	0·74	- 0	45	300	29	15	300	29	17	48	29	6 2749·0
128	301	4	55	67	27·80	- 28	39	300	36	16						
129	301	4	55	67	27·61	- 28	27	300	36	28						
131	300	54	55	67	18·32	- 18	53	300	36	2	300	36	15			
125	37	20	5	67	15·66	+ 16	18	37	36	13						
124	37	30	5	70	6·09	+ 6	15	37	36	20	37	36	17	48	30	1 2749·7
229	37	30	0	86	2·96	+ 2	59	37	32	59						
230	300	35	0	86	11·25	- 11	20	300	23	40						
231	300	30	0	86	6·27	- 6	19	300	23	41	300	23	40	48	34	39 2753·0
229	37	30	0	86	6·42	+ 6	28	37	36	28						
230	300	35	0	86	14·71	- 14	49	300	20	11						
231	300	30	0	86	9·74	- 9	49	300	20	11	300	20	11	48	38	9 2755·5
197	300	59	55	65	31·13	- 32	9	300	27	44						
198	301	10	0	65	41·00	- 42	21	300	27	39	300	27	41			
200	37	3	0	65	39·44	+ 40	44	37	43	44						
201	37	12	55	65	29·76	+ 31	23	37	44	18	37	44	1	48	38	10 2755·5
197	300	59	55	65	47·45	- 49	0	300	10	55						
198	301	10	0	65	57·22	- 59	6	300	10	54	300	10	54			
200	37	3	0	65	55·57	+ 57	23	38	0	23						
201	37	12	55	65	45·88	+ 48	23	38	1	18	38	0	51	48	54	58 (2767·3)

I	II	III	IV	V	VI	VII	VIII	IX
			hundredths of an inch					wave- length
220	299 35 0	79	27.90	+28 20	300 3 20			
221	299 35 0	79	27.82	+28 15	300 3 15	300 3 18		
222	38 30 0	79	36.45	-37 1	37 52 59			
218	38 30 0	79	36.32	-36 53	37 53 7			
219	38 25 0	79	31.56	-32 3	37 52 57	37 53 2	48 54 52	2767.2
286	38 20 0	84	26.85	-27 7	37 52 53			
287	299 40 0	84	23.15	+23 23	300 3 23		48 54 45	(2767.1)
286	38 20 0	84	10.20	-10 18	38 9 42			
287	299 40 0	84	6.27	+ 6 20	299 46 20		49 11 41	2779.0
220	299 35 0	79	11.26	+11 27	299 46 27			
221	299 35 0	79	11.16	+11 20	299 46 20	299 46 24		
222	38 30 0	79	19.96	-20 16	38 9 44			
218	38 30 0	79	19.78	-20 5	38 9 55			
219	38 25 0	79	14.98	-15 13	38 9 47	38 9 51	49 11 43	2779.0
220	299 35 0	79	5.06	+ 5 8	299 40 8			
221	299 35 0	79	4.95	+ 5 2	299 40 2	299 40 5		
222	38 30 0	79	13.80	-14 1	38 15 59			
218	38 30 0	79	13.62	-13 51	38 16 9			
219	38 25 0	79	8.84	- 8 59	38 16 1	38 16 3	49 17 59	2783.4
286	38 20 0	84	3.97	- 4 1	38 15 59			
287	299 40 0	84	0.05	+ 0 3	299 40 3		49 17 58	2783.4
321	39 0 0	86	20.58	-20 43	38 39 17			
322	298 55 0	86	23.65	+23 49	299 18 49		49 40 14	2798.8
321	39 0 0	86	0.52	- 0 31	38 59 29			
322	298 55 0	86	3.26	+ 3 17	298 58 17		50 0 36	2812.9
321	39 0 0	86	25.93	+26 7	39 26 7			
322	298 55 0	86	23.26	-23 26	298 31 34		50 27 17	2831.1
281	298 25 0	87	5.95	+ 5 59	298 30 59			
284	298 25 0	87	5.81	+ 5 51	298 30 51	298 30 55		
282	39 35 0	87	9.27	- 9 20	39 25 40			
283	39 35 0	87	9.74	- 9 48	39 25 12			
285	39 35 0	87	9.60	- 9 40	39 25 20	39 25 24	50 27 14	(2831.0)
281	298 25 0	87	0.13	- 0 8	298 24 52			
284	298 25 0	87	0.36	- 0 22	298 24 38	298 24 45		
282	39 35 0	87	3.20	- 3 13	39 31 47			
283	39 35 0	87	2.71	- 2 44	39 32 16			
285	39 35 0	87	3.58	- 3 36	39 31 24	39 31 49	50 33 32	2835.3
281	298 25 0	87	7.47	- 7 31	298 17 29			
284	298 25 0	87	7.59	- 7 38	298 17 22	298 17 25		
282	39 35 0	87	3.99	+ 4 1	39 39 1			
283	39 35 0	87	4.54	+ 4 31	39 39 34			
285	39 35 0	87	3.58	+ 3 36	39 38 36	39 39 5	50 40 50	2840.3
288	297 25 0	88	25.62	+25 45	297 50 45			
289	40 35 0	88	30.28	-30 26	40 4 26		51 6 51	(2857.8)

I	II			III	IV	V	VI	VII	VIII	IX	
	°	'	"		hundredths of an inch	'	"	°	'	"	wave- length
318	297	20	0	88	31·35	+31	30	297	51	30	2857·9
319	297	20	0	88	31·40	+31	33	297	51	33	
320	40	30	0	88	23·73	-23	51	40	6	9	(2858·1)
278	40	35	0	88	29·57	-29	43	40	5	17	
279	297	25	0	88	26·13	+26	16	297	51	16	
280	297	25	0	88	26·34	+26	28	297	51	28	(2857·8)
278	40	35	0	88	8·62	-8	40	40	26	20	
280	297	25	0	88	5·29	+5	19	297	30	19	51 28 0 (2871·9)
288	297	25	0	88	4·54	+4	34	297	29	34	
289	40	35	0	88	9·45	-9	30	40	25	30	51 27 58 (2871·9)
318	297	20	0	88	10·37	+10	25	297	30	25	2872·0
319	297	20	0	88	10·34	+10	24	297	30	24	
320	40	30	0	88	2·77	-2	47	40	27	13	51 28 24 (2872·2)
269	40	50	0	91	21·93	-21	58	40	28	2	
270	40	55	0	91	27·00	-27	2	40	27	58	40 28 0
271	297	10	0	91	18·96	+18	59	297	28	59	
272	297	5	0	91	23·94	+23	59	297	28	59	51 29 30 (2872·9)
288	297	25	0	88	3·02	+3	2	297	28	2	
289	40	35	0	88	7·86	-7	54	40	27	6	51 29 32 (2872·9)
317	297	25	0	88	3·94	+3	58	297	28	58	2873·0
318	297	20	0	88	8·93	+8	59	297	28	59	
319	297	20	0	88	8·86	+8	54	297	28	54	297 28 57
320	40	30	0	88	1·36	-1	22	40	28	38	51 29 51 (2873·1)
278	40	35	0	88	7·12	-7	9	40	27	51	
279	297	25	0	88	3·47	+3	29	297	28	29	
280	297	25	0	88	3·78	+3	48	297	28	48	297 28 39 51 29 36 2873·0
278	40	35	0	88	3·82	+3	50	40	38	50	
280	297	25	0	88	7·58	-7	37	297	17	23	51 40 48 2880·4
269	40	50	0	91	10·94	-10	58	40	39	2	
270	40	55	0	91	15·99	-16	1	40	38	59	40 39 0
271	297	10	0	91	7·66	+7	40	297	17	40	
272	297	5	0	91	12·56	+12	35	297	17	35	297 17 38 51 40 41 (2880·3)
288	297	25	0	88	8·12	-8	10	297	16	50	
289	40	35	0	88	3·18	+3	12	40	38	12	51 40 41 (2880·3)
317	297	25	0	88	7·28	-7	19	297	17	41	
318	297	20	0	88	2·56	-2	34	297	17	26	
319	297	20	0	88	2·46	-2	28	297	17	32	297 17 33
320	40	30	0	88	9·75	+9	48	40	39	48	51 41 7 (2880·6)
269	40	50	0	91	6·50	-6	31	40	43	29	
270	40	55	0	91	11·55	-11	34	40	43	26	40 43 27
271	297	10	0	91	3·21	+3	13	297	13	13	
273	297	5	0	91	8·14	+8	12	297	13	12	297 13 12 51 45 7 2883·3

I	II	III	IV	V	VI	VII	VIII	IX
	° ' "		hundredths of an inch	' "	° ' "	° ' "	° ' "	wave- length
278	40 35 0	88	8.17	+ 8 13	40 43 13			
279	297 25 0	88	11.92	- 11 59	297 13 1			
280	297 25 0	88	11.84	- 11 54	297 13 6	297 13 3	51 45 5	2883.3
288	297 25 0	88	12.53	- 12 36	297 12 24			
289	40 35 0	88	7.52	+ 7 34	40 42 34		51 45 5	2883.3
317	297 25 0	88	11.59	- 11 39	297 13 21			
318	297 20 0	88	6.95	- 6 59	297 13 1			
319	297 20 0	88	6.77	- 6 48	297 13 12	297 13 11		
320	40 30 0	88	14.13	+ 14 12	40 44 12		51 45 31	(2883.5)
275	296 10 0	93	2.48	- 2 29	296 7 32			
276	41 50 0	93	0.91	- 0 55	41 49 5			
277	41 55 0	93	6.00	- 6 1	41 48 59	41 49 2	52 50 45	(2926.1)
267	296 10 0	93	2.85	- 2 51	296 7 9			
268	41 50 0	93	1.20	- 1 12	41 48 48		52 50 50	2926.0
310	41 55 0	93	10.19	+ 10 11	42 5 11			
311	41 50 0	93	15.00	+ 14 59	42 4 59	42 5 5		
312	296 0 0	93	8.16	- 8 9	295 51 51		53 6 37	2928.3
267	296 10 0	93	30.58	- 30 33	295 39 27			
268	41 50 0	93	26.50	+ 26 29	42 16 29		53 18 31	(2943.9)
275	296 10 0	93	30.48	- 30 27	295 39 33			
276	41 50 0	93	26.78	+ 26 45	42 16 45			
277	41 55 0	93	21.73	+ 21 43	42 16 43	42 16 44	53 18 36	2944.0
310	41 55 0	93	21.95	+ 21 56	42 16 56			
311	41 50 0	93	26.75	+ 26 44	42 16 44	42 16 50		
212	296 0 0	93	20.04	- 20 1	295 39 59			
315	296 0 0	93	19.97	- 19 57	295 40 3	295 40 1	53 18 25	(2943.9)
275	296 10 0	93	35.50	- 35 28	295 34 32			
276	41 50 0	93	31.94	+ 31 55	42 21 55			U
277	41 55 0	93	26.89	+ 26 52	42 21 52	42 21 54	53 23 41	2947.3

As in the highest region we have used the lines in the spectrum of the spark between copper electrodes as lines of reference, we add here the measurements and calculated values for these lines, and for the strong magnesium lines which we have sometimes used in interpolating.

COPPER LINES.

I	II	III	IV	V	VI	VII	VIII	IX
			hundredths of an inch					wave- length
327	312 55 0	24	27·88	+30 17	313 25 17			
330	313 5 0	24	18·19	+19 46	313 24 46			
331	313 5 0	24	18·81	+20 26	313 25 26	313 25 10		
328	25 0 0	24	23·96	-26 2	24 33 58			
329	24 45 0	24	10·30	-11 11	24 33 49	24 33 53	35 34 21	2135·7
327	312 55 0	24	13·87	+15 4	313 10 4			
330	313 5 0	24	4·17	+ 4 32	313 9 32			
331	313 5 0	24	4·73	+ 5 8	313 10 8	313 9 55		
328	25 0 0	24	10·15	-11 2	24 48 58			
329	24 45 0	24	3·53	+ 3 50	24 48 50	24 48 54	35 49 30	2148·9
297	25 50 0	31	24·22	-26 5	25 23 55			
298	312 10 0	31	23·66	+25 29	312 35 29		36 24 13	2178·8
297	25 50 0	31	13·18	-14 11	25 35 49			
298	312 10 0	31	12·24	+13 11	312 23 11		36 36 19	2189·2
325	26 0 0	31	22·94	-24 42	25 35 18			
326	311 55 0	31	25·83	+27 49	312 22 49		36 36 14	2189·2
325	26 0 0	31	20·02	-21 33	25 38 27			
326	311 55 0	31	22·98	+24 45	312 19 45		36 39 21	2191·8
297	25 50 0	31	10·32	-11 7	25 38 53			
298	312 10 0	31	9·37	+10 5	312 20 5		36 39 24	(2191·9)
297	25 50 0	31	2·37	- 2 33	25 47 27			
298	312 10 0	31	1·46	+ 1 34	312 11 34		36 47 56	2199·2
325	26 0 0	31	0·65	- 0 42	25 59 18			
326	311 55 0	31	3·19	+ 3 26	311 58 26		37 0 26	(2209·9)
291	26 25 0	37	23·62	-25 15	25 59 45			
293	26 35 0	37	33·52	-35 55	25 59 5			
296	26 25 0	34	23·27	-24 55	26 0 5			
297	25 50 0	31	9·08	+ 9 47	25 59 47	25 59 40		
298	312 10 0	31	10·19	-10 58	311 59 2			
299	311 10 0	39	46·93	+50 2	312 0 2			2209·7
294	311 25 0	37	31·70	+33 53	311 58 53			
295	311 35 0	34	22·73	+24 23	311 59 23	311 59 20	37 0 10	(2209·6)
291	26 25 0	37	15·26	-16 19	26 8 41			
293	26 35 0	37	24·69	-26 27	26 8 33			
296	26 25 0	34	14·80	-15 53	26 9 7			
297	25 50 0	31	17·55	+18 54	26 8 54			
300	26 50 0	39	39·24	-41 50	26 8 10	26 8 41		
294	311 25 0	37	22·94	+24 31	311 49 31			
295	311 35 0	34	14·04	+15 4	311 50 4			2217·5
298	312 10 0	31	18·77	-20 13	311 49 47			
299	311 10 0	39	37·91	+40 25	311 50 25	311 49 57	37 9 22	
325	26 0 0	31	7·68	+ 8 16	26 8 16			
326	311 55 0	31	5·40	- 5 49	311 49 11		37 9 33	(2217·6)

COPPER LINES—(continued).

I	II	III	IV	V	VI	VII	VIII	IX
			hundredths of an inch					wave- length
291	26 25 0	37	3.49	-- 3 44	26 21 16			
293	26 35 0	37	12.99	-13 55	26 21 5			
296	26 25 0	34	3.05	- 3 16	26 21 44			
300	26 50 0	39	27.23	-29 2	26 20 58	26 21 16		
294	311 25 0	37	10.95	+11 42	311 36 42			
295	311 35 0	34	1.87	+ 2 0	311 37 0			
299	311 10 0	39	25.85	+27 33	311 37 33	311 37 5	37 22 5	2228.3
293	26 35 0	37	11.58	-12 24	26 22 36			
296	26 25 0	34	1.65	- 1 46	26 23 14	26 22 55		
294	311 25 0	37	9.51	+10 10	311 35 10			
295	311 35 0	34	0.51	+ 0 32	311 35 32			
299	311 10 0	39	24.52	+26 8	311 36 8	311 35 37	37 23 39	2229.6
291	26 25 0	37	11.59	+12 23	26 37 23			
292	26 30 0	38	7.30	+ 7 47	26 37 47			
293	26 35 0	37	2.15	+ 2 18	26 37 18			
296	26 25 0	34	12.00	+12 52	26 37 52			
300	26 50 0	39	11.52	-12 17	26 37 43	26 37 37		
294	311 25 0	37	4.54	- 4 51	311 20 9			
295	311 35 0	34	13.28	-14 15	311 20 45			
299	311 10 0	39	10.15	+10 49	311 20 49	311 20 34	37 38 31	2242.2
332	27 0 0	39	20.54	-21 54	26 38 6			
333	26 55 0	39	15.96	-17 1	26 37 59	26 38 2		
334	310 55 0	39	24.32	+25 56	311 20 56			
335	311 0 0	39	19.70	+20 49	311 20 49	311 20 53	37 38 34	2242.2
332	27 0 0	39	15.77	-16 49	26 43 11			
333	26 55 0	39	11.03	-11 46	26 43 14	26 43 12		
334	310 55 0	39	19.47	+20 46	311 15 46			
335	311 0 0	39	14.61	+15 27	311 15 27	311 15 37	37 43 47	2246.6
291	26 25 0	37	16.48	+17 37	26 42 37			
292	26 30 0	38	12.16	+12 59	26 42 59			
293	26 35 0	37	7.03	+ 7 32	26 42 32			
296	26 25 0	34	16.80	+18 1	26 43 1			
300	26 50 0	39	6.62	- 7 3	26 42 57	26 42 49		
294	311 25 0	37	9.45	-10 6	311 14 54			
295	311 35 0	34	18.20	-19 31	311 15 29			
299	311 10 0	39	5.31	+ 5 40	311 15 40	311 15 21	37 43 44	2246.6
332	27 0 0	39	2.98	+ 3 10	27 3 10			
333	26 55 0	39	7.80	+ 8 19	27 3 19	27 3 15		
335	311 0 0	39	4.27	- 4 31	310 55 29		38 3 53	2263.6
332	27 0 0	39	16.90	+18 1	27 18 1			
333	26 55 0	39	21.60	+23 2	27 18 2			
334	310 55 0	39	13.52	-14 25	310 40 35			
335	311 0 0	39	18.18	-19 13	310 40 47			
336	310 30 0	46	10.33	+10 55	310 40 55			
337	310 25 0	46	15.12	+15 59	310 40 59	310 40 49		
338	27 30 0	46	11.24	-11 53	27 18 7			
340	27 35 0	46	16.00	-16 55	27 18 5			
339	27 25 0	46	6.71	- 7 6	27 17 54	27 18 2	38 18 37	2276.0

COPPER LINES—(continued).

I	II			III	IV	V	VI			VII			VIII			IX		
	°	'	"		hundredths of an inch	°	'	"	°	'	"	°	'	"	°	'	"	wave- length
291	26	25	0	27	48.59	+51	56		27	16	56							
292	26	30	0	38	44.59	+47	36		27	17	36							
293	26	35	0	37	39.99	+42	51		27	17	51							
296	26	25	0	34	48.64	+52	11		27	17	11							
300	26	50	0	39	26.44	+28	11		27	18	11	27	17	38				
294	311	25	0	37	42.01	-44	54	310	40	6								
295	311	35	0	34	50.70	-54	23	310	40	37								
299	311	10	0	39	27.31	-29	7	310	40	53	310	40	32	38	18	33	(2275.9)	
336	310	30	0	46	10.33	-10	55	310	19	5								
337	310	25	0	46	5.55	-5	52	310	19	8	310	19	6					
338	27	30	0	46	9.30	+9	50	27	39	50								
340	27	35	0	46	4.40	+4	39	27	39	39								
339	27	25	0	46	13.76	+14	33	27	39	33	27	39	41	38	40	19	2294.1	

MAGNESIUM LINES.

I	II			III	IV	V			VI			VII			VIII			IX
	°	'	"		hundredths of an inch	°	'	"	°	'	"	°	'	"	°	'	"	wave- length
129	301	4	55	67	68.67	-1	10	45	299	54	10							
128	301	4	55	67	68.85	-1	10	58	299	53	57							
131	300	54	55	67	59.32	-1	1	7	299	53	48	299	54	4				
134	300	4	55	75	10.67	-0	10	53	299	54	2							
135	300	4	55	75	10.39	-0	10	36	299	54	19							
139	300	0	3	72	5.66	-0	5	47	299	54	16							
140	300	0	3	72	5.95	-0	6	6	299	53	57							
137	38	10	0	75	8.75	+0	8	56	38	18	56							
138	38	15	0	72	3.42	+0	3	30	38	18	30							
125	37	20	5	67	56.82	+0	58	32	38	18	37							
121	37	30	5	70	47.33	+0	48	35	38	18	40	38	18	41	49	12	19	2779.4
137	38	10	0	75	30.88	+0	31	31	38	41	31							
138	38	15	0	72	25.68	+0	26	18	38	41	18	38	41	25				
139	300	0	3	72	27.86	-0	28	32	299	31	31							
140	300	0	3	72	28.02	-0	28	42	299	31	21	299	31	26	49	35	0	2795.2
306	299	15	0	86	8.75	+0	8	49	299	23	49	299	23	50				
307	38	45	0	86	10.89	-0	11	1	38	33	59							
308	38	30	0	85	3.84	+0	3	52	38	33	52	38	33	55				
309	299	30	0	85	6.10	-0	6	9	299	23	51				49	35	2	2795.2
137	38	10	0	75	41.09	+0	41	56	38	51	56							
138	38	15	0	72	35.83	+0	36	42	38	51	42	38	51	49				
139	300	0	3	72	37.82	-0	38	44	299	21	19							
140	300	0	3	72	38.21	-0	39	8	299	20	55	299	21	7	49	45	21	2802.4
306	299	15	0	86	1.57	-0	1	35	299	13	25							
307	38	45	0	86	0.59	-0	0	36	38	44	24							
308	38	30	0	85	14.16	+0	14	17	38	44	17	38	44	21				
309	299	30	0	85	16.48	-0	16	37	299	13	23	299	13	24	49	45	28	(2802.5)
303	40	0	0	85	2.97	-0	3	0	39	57	0							
304	298	0	0	85	0.34	+0	0	21	298	0	21							
305	298	5	0	85	4.48	-0	4	31	298	0	29	298	0	25	50	58	18	2852.0

Remarks on the foregoing tables.

It will be observed that when two or more independent determinations have been made the wave-lengths found are often identical, rarely differ by more than $\cdot 2$ of a tenth-metre. This seems to make the probable error in most cases very small—smaller than we venture to think it really may be, for there are one or two sources of error which are quite sufficient to account for a variation of $\cdot 2$ of a tenth-metre in the wave-length. First the sliding tubes of the telescope, for it has a draw tube as well as the usual rack and pinion arrangement for focussing, in order to allow for the great variations in the focal distance of the uncorrected quartz lenses, and such sliding tubes have always some play, so that in the operation of reversing the photographic plate by turning the sliding tube about its axis there might easily be a small displacement. Indeed, the measurement of plates taken successively without movement of any part of the apparatus, except the photographic slide, shewed that there was such a displacement of the axis, and that it might make an error of $\pm 10''$ in the measurement of the angle, or $\pm \cdot 13$ on an average in the value of the wave-length.

Another source of error is the want of sharp definition of some of the lines. Some of the lines are really diffuse, and in every case, as already observed, if the image is correctly focussed on the plate when the telescope is on one side of the collimator, it is always a little out of focus when the telescope is moved round to the other side. Hence there is a possible error in measuring the distance between the lines which may easily amount to $\pm 8''$ of angular measure, or $\pm \cdot 1$ in the value of the wave-length,

Still we do not think the probable error exceeds $\pm \cdot 25$ of a tenth-metre.

Determination of the intermediate lines.

The wave-lengths of a sufficient number of lines of reference having been measured by the grating, the intermediate lines have been mapped by means of prisms. For this part of the work a calcite prism of 30° , cut so that one face is perpendicular to the axis of the crystal, was fixed to the end of the collimator, and a similar prism to the end of the telescope, while between them another calcite prism of 60° , cut so that the faces are equally inclined to the axis of the crystal, was maintained by a simple system of linkage at the position of minimum deviation, which is also that of single refraction. Photographs were taken at short intervals all down the scale of the spectrum of the arc and spark simultaneously. The image of the arc was focussed on the slit by the quartz lens already mentioned, and thrown just under the centre. At the same time the spark was made to pass horizontally close in front of the slit, without the interposition of a lens, but just above the centre. In this way two images were impressed on the plate overlapping one another

in the middle. The distances between the lines was afterwards measured under the microscope, and the inverse squares of the wave-lengths of the intermediate lines deduced by the graphic method of interpolation between those of the lines of reference. A table of inverse squares was used for the reduction to simple wave-lengths.

The following table gives the results. In many cases there is much difference in the relative intensities of the same line in the arc and spark, and in some cases lines are visible in the photograph of the arc which are not in that of the spark, and *vice versa*. Beyond the wave-length 2327 no spark lines seem to have made any impression on the plates, but the arc lines continue with, however, a sensible falling off in intensity up to the end of the region observed. For this region the copper lines of reference were used, as already explained, and for the highest part of it, above wave-length 2230, quartz prisms were substituted for those of calcite with advantage as regards the amount of light transmitted, but with some loss of dispersion and more of definition.

In the following table the second column gives the wave-length, and the lines marked with a "c" are probably carbon lines, the first gives approximately the relative intensities with which the lines are impressed on the photographic plates, 1 representing the strongest and 6 the weakest lines. It also indicates whether the line is an arc or a spark-line, *a* indicating arc-lines; *s*, spark-lines. Thus 3 *a* 1 *s* before a line indicates that its intensity in arc is 3, in spark, 1; 6 *a* indicates a line which is in arc only and of intensity 6; 2 *a* *s* indicates a line of intensity 2 in both arc and spark.

LIST OF ULTRA-VIOLET IRON LINES.

6 <i>a</i>	2167·4	3 <i>a</i>	2229·7	5 <i>a</i>	2264·2	5 <i>a</i>	2283·0
6 <i>a</i>	2171·7	6 <i>a</i>	2230·9	5 <i>a</i>	2264·7	5 <i>a</i>	2283·2
6 <i>a</i>	2173·4	6 <i>a</i>	2240·2	6 <i>a</i>	2265·7	4 <i>a</i>	2283·6
6 <i>a</i>	2177·0	6 <i>a</i>	2242·2	6 <i>a</i>	2266·6	3 <i>a</i>	2284·0
6 <i>a</i>	2178·0	6 <i>a</i>	2243·9	5 <i>a</i>	2266·8	3 <i>a</i>	2287·1
6 <i>a</i>	2181·5	5 <i>a</i>	2245·3	3 <i>a</i>	2267·2	3 <i>a</i>	2287·4
6 <i>a</i>	2183·7	4 <i>a</i>	2248·5	6 <i>a</i>	2268·8	6 <i>a</i>	2287·9
6 <i>a</i>	2186·1	4 <i>a</i>	2248·8	4 <i>a</i>	2270·5	3 <i>a</i>	2288·8
6 <i>a</i>	2186·8	4 <i>a</i>	2250·5	4 <i>a</i>	2271·5	5 <i>a</i>	2289·9
6 <i>a</i>	2191·3	6 <i>a</i>	2250·6	4 <i>a</i>	2271·8	4 <i>a</i>	2290·3
5 <i>a</i>	2195·5	6 <i>a</i>	2251·2	4 <i>a</i>	2272·5	6 <i>a</i>	2290·6
5 <i>a</i>	2199·3	6 <i>a</i>	2251·6	4 <i>a</i>	2273·8	4 <i>a</i>	2290·9
6 <i>a</i>	2200·0	4 <i>a</i>	2252·8	4 <i>a</i>	2274·9	6 <i>a</i>	2291·4
6 <i>a</i>	2200·2	4 <i>a</i>	2255·4	6 <i>a</i>	2275·2	3 <i>a</i>	2292·3
4 <i>a</i>	2207·5	4 <i>a</i>	2259·2	4 <i>a</i>	2275·7	3 <i>a</i>	2293·6
4 <i>a</i>	2210·4	4 <i>a</i>	2259·8	4 <i>a</i>	2276·9	3 <i>a</i>	2294·2
6 <i>a</i>	2211·4	5 <i>a</i>	2260·4	4 <i>a</i>	2277·5	3 <i>a</i>	2296·8
4 <i>a</i>	2214·1	5 <i>a</i>	2260·7	3 <i>a</i>	2279·7	3 <i>a</i>	2297·6
3 <i>a</i>	2216·2	6 <i>a</i>	2262·4	4 <i>a</i>	2280·0	3 <i>a</i>	2298·0
4 <i>a</i>	2225·2	6 <i>a</i>	2262·8	6 <i>a</i>	2281·8	4 <i>a</i>	2298·6
3 <i>a</i>	2227·3	6 <i>a</i>	2263·2	6 <i>a</i>	2282·8	3 <i>a</i>	2299·0

LIST OF ULTRA-VIOLET IRON LINES (*continued*).

6 <i>a</i>	2299.2	6 <i>a</i> 5 <i>s</i>	2355.1	6 <i>s</i>	2398.5	4 <i>a</i>	2437.9
3 <i>a</i>	2300.0	6 <i>a</i>	2355.6	1 <i>a s</i>	2399.0	2 <i>s</i>	2439.0
5 <i>a</i>	2300.4	4 <i>s</i>	2356.7	6 <i>a</i> 2 <i>s</i>	2400.0	2 <i>a</i> 6 <i>s</i>	2439.4
4 <i>a</i>	2301.0	1 <i>a s</i>	2358.7	6 <i>a s</i>	2401.0	3 <i>a</i>	2439.8
3 <i>a</i>	2301.4	6 <i>a s</i>	2359.2	6 <i>a</i>	2401.4	3 <i>s</i>	2440.1
3 <i>a</i>	2303.2	2 <i>a</i> 1 <i>s</i>	2359.7	6 <i>a</i> 5 <i>s</i>	2401.9	6 <i>s</i>	2441.0
3 <i>a</i>	2303.4	2 <i>a</i> 1 <i>s</i>	2359.9	6 <i>a</i> 5 <i>s</i>	2402.3	6 <i>a</i>	2441.5
5 <i>a</i>	2304.4	6 <i>a</i>	2360.3	3 <i>a s</i>	2404.2	2 <i>a</i> 5 <i>s</i>	2442.3
5 <i>a</i>	2305.8	6 <i>s</i>	2361.3	1 <i>a s</i>	2404.5	3 <i>a</i> 6 <i>s</i>	2443.7
4 <i>a</i>	2306.0	4 <i>a</i> 3 <i>s</i>	2361.6	6 <i>s</i>	2405.5	5 <i>a</i> 1 <i>s</i>	2444.3
2 <i>a</i>	2308.6	6 <i>s</i>	2362.9	1 <i>a s</i>	2406.3	6 <i>a s</i>	2444.9
6 <i>a</i>	2309.3	3 <i>s</i>	2363.3	6 <i>s</i>	2406.6	6 <i>a</i> 3 <i>s</i>	2445.4
6 <i>a</i>	2310.6	3 <i>s</i>	2363.5	6 <i>a</i>	2406.9	6 <i>s</i>	2445.9
5 <i>a</i>	2311.0	2 <i>a</i> 1 <i>s</i>	2364.4	6 <i>a</i>	2407.3	6 <i>a</i> 3 <i>s</i>	2446.3
6 <i>a</i>	2311.6	6 <i>a</i>	2365.1	6 <i>a s</i>	2407.6	3 <i>s</i>	2447.1
6 <i>a</i>	2312.0	5 <i>s</i>	2365.3	6 <i>s</i>	2408.4	3 <i>a s</i>	2447.5
2 <i>a</i>	2312.7	3 <i>a s</i>	2366.2	1 <i>a s</i>	2410.2	6 <i>a</i>	2448.1
6 <i>a</i>	2313.6	2 <i>a</i> 1 <i>s</i>	2368.2	1 <i>a s</i>	2410.7	6 <i>a</i>	2448.5
6 <i>a</i>	2316.7	4 <i>a</i>	2369.1	6 <i>a</i>	2411.4	4 <i>s</i>	2449.6
5 <i>a</i>	2317.5	5 <i>s</i>	2369.6	1 <i>a s</i>	2413.0	6 <i>a</i> 4 <i>s</i>	2450.0
6 <i>a</i>	2317.7	4 <i>a s</i>	2370.1	6 <i>a s</i>	2413.8	6 <i>a</i>	2450.7
5 <i>a</i>	2319.2	4 <i>a</i>	2371.1	6 <i>a s</i>	2414.8	6 <i>a</i> 5 <i>s</i>	2451.0
6 <i>a</i>	2319.6	4 <i>s</i>	2372.3	6 <i>a</i>	2415.4	6 <i>a</i>	2451.3
3 <i>a</i>	2319.9	6 <i>a</i>	2372.7	6 <i>a</i> 5 <i>s</i>	2416.3	6 <i>a</i>	2451.8
2 <i>a</i> 1 <i>s</i>	2326.9	4 <i>s</i>	2373.3	6 <i>a</i>	2417.1	6 <i>a</i>	2452.3
6 <i>a</i>	2329.3	2 <i>a</i> 1 <i>s</i>	2373.4	6 <i>a</i> 2 <i>s</i>	2417.5	6 <i>s</i>	2452.9
2 <i>a</i> 1 <i>s</i>	2330.9	6 <i>a</i>	2374.1	6 <i>a</i> 5 <i>s</i>	2418.2	3 <i>a</i>	2453.2
2 <i>a</i> 1 <i>s</i>	2332.5	2 <i>a</i> 1 <i>s</i>	2374.9	3 <i>a</i>	2418.9	5 <i>s</i>	2453.5
6 <i>a</i>	2333.1	6 <i>a</i> 3 <i>s</i>	2376.2	6 <i>a</i>	2419.4	6 <i>s</i>	2453.8
6 <i>a</i>	2334.2	6 <i>a</i>	2376.9	6 <i>s</i>	2419.7	3 <i>s</i>	2454.3
6 <i>a</i>	2334.5	6 <i>a</i>	2377.6	6 <i>a</i>	2420.0	6 <i>a</i>	2455.3
6 <i>a</i>	2334.8	6 <i>s</i>	2378.2	6 <i>a</i>	2420.7	6 <i>s</i>	2455.7
2 <i>a</i> 1 <i>s</i>	2337.7	6 <i>s</i>	2378.8	6 <i>a</i>	2421.3	6 <i>a</i>	2456.0
2 <i>a</i> 6 <i>s</i>	2339.0	2 <i>a</i> 1 <i>s</i>	2379.0	6 <i>a</i> 3 <i>s</i>	2422.4	6 <i>s</i>	2456.4
3 <i>a</i>	2339.3	2 <i>a</i> 1 <i>s</i>	2380.5	6 <i>a</i> 4 <i>s</i>	2422.9	2 <i>a</i> 5 <i>s</i>	2457.4
5 <i>a</i> 6 <i>s</i>	2340.0	1 <i>a s</i>	2381.7	5 <i>a</i> 1 <i>s</i>	2423.8	6 <i>a</i>	2458.2
6 <i>a</i>	2341.2	3 <i>a s</i>	2382.7	6 <i>s</i>	2424.3	6 <i>a</i> 1 <i>s</i>	2458.5
6 <i>s</i>	2341.6	2 <i>a s</i>	2383.0	6 <i>a s</i>	2425.0	6 <i>a</i> 4 <i>s</i>	2460.2
6 <i>s</i>	2341.8	2 <i>a s</i>	2384.2	6 <i>a</i> 5 <i>s</i>	2425.4	6 <i>a</i>	2460.8
1 <i>a s</i>	2343.1	6 <i>a</i> 5 <i>s</i>	2384.8	6 <i>s</i>	2427.0	6 <i>a</i> 3 <i>s</i>	2461.0
6 <i>a</i> 5 <i>s</i>	2343.6	6 <i>a</i>	2385.8	2 <i>s</i>	2427.9	3 <i>s</i>	2461.4
4 <i>a</i> 3 <i>s</i>	2343.9	4 <i>s</i>	2386.3	6 <i>a s</i>	2428.5	3 <i>a</i>	2461.9
4 <i>a</i>	2344.7	6 <i>a</i> 4 <i>s</i>	2387.2	6 <i>s</i>	2428.7	2 <i>a</i> 6 <i>s</i>	2462.3
3 <i>s</i>	2344.9	6 <i>s</i>	2388.0	6 <i>a s</i>	2429.0	6 <i>a</i> 4 <i>s</i>	2462.8
6 <i>a s</i>	2345.9	1 <i>a s</i>	2388.4	3 <i>a</i> 2 <i>s</i>	2429.7	5 <i>a</i>	2463.4
6 <i>s</i>	2346.4	6 <i>s</i>	2389.2	6 <i>a s</i>	2430.5	4 <i>s</i>	2463.7
1 <i>a s</i>	2347.8	3 <i>a</i>	2389.9	6 <i>a</i>	2430.7	4 <i>s</i>	2464.5
1 <i>a s</i>	2348.0	5 <i>s</i>	2390.1	6 <i>a</i> 2 <i>s</i>	2431.8	3 <i>a</i> 4 <i>s</i>	2464.7
6 <i>s</i>	2349.0	6 <i>s</i>	2390.7	2 <i>s</i>	2432.5	3 <i>s</i>	2465.4
6 <i>a</i>	2349.5	3 <i>a</i> 4 <i>s</i>	2391.3	4 <i>s</i>	2433.2	5 <i>a</i> 2 <i>s</i>	2466.4
6 <i>a s</i>	2349.9	6 <i>a s</i>	2392.4	6 <i>a s</i>	2433.9	5 <i>a</i>	2467.2
6 <i>a</i> 2 <i>s</i>	2350.9	6 <i>a</i>	2392.8	6 <i>a</i> 3 <i>s</i>	2434.3	5 <i>s</i>	2467.8
6 <i>a s</i>	2351.5	6 <i>a</i>	2394.1	5 <i>a</i> 3 <i>s</i>	2434.7	3 <i>a</i> 6 <i>s</i>	2468.4
6 <i>s</i>	2352.1	6 <i>s</i>	2394.7	6 <i>a s</i>	2435.6	3 <i>s</i>	2469.0
5 <i>s</i>	2353.3	3 <i>a s</i>	2395.2	6 <i>a s</i>	2436.0	2 <i>s</i>	2470.3
6 <i>a</i> 3 <i>s</i>	2354.1	1 <i>a s</i>	2395.4	5 <i>s</i>	2436.4	6 <i>a</i>	2470.5
3 <i>a s</i>	2354.6	5 <i>s</i>	2396.5	5 <i>s</i>	2436.9	3 <i>a</i> 4 <i>s</i>	2471.9
5 <i>s</i>	2354.8	6 <i>a</i>	2398.0	6 <i>s</i>	2437.3	2 <i>a</i> 5 <i>s</i>	2472.4

LIST OF ULTRA-VIOLET IRON LINES—(continued).

6 a	2472.7	5 s	c 2508.8	6 s	2547.0	2 a	6 s	2584.0	
5 s	2472.9	2 a	5 s	2510.6	6 a	5 s	1 a s	2585.4	
3 a s	2474.5	6 a	1 s	c 2511.4	5 s	2548.4	3 a s	2587.5	
6 s	2474.9	6 a	2511.6	5 s	2549.0	6 s	2588.2		
6 s	2475.5	3 a	2512.0	5 s	2549.1	6 s	2590.0		
6 a	2475.8	3 a	4 s	2512.2	2 a	2549.2	3 a s	2591.0	
6 s	2476.0	6 a	2513.2	5 s	2549.7	6 a	2591.7		
5 a	6 s	3 a s	c 2514.1	5 s	2550.3	3 s	2592.2		
5 s	2477.1	6 a	2514.3	6 a s	2550.8	3 a s	2593.1		
6 s	2477.9	4 s	2514.7	6 a	2552.3	6 a	2593.5		
1 a	3 s	1 a	6 s	c 2515.8	6 a s	2552.8	6 s	2594.5	
6 s	2479.0	6 a	2516.3	6 s	2553.4	6 a	2595.2		
6 a	2479.2	6 a	3 s	2516.8	5 s	2554.8	6 a	2596.0	
2 a	6 s	5 a	2517.4	6 a	2554.9	1 a s	2597.8		
6 a	2 s	3 a	6 s	2517.8	5 s	2555.2	1 a s	2598.9	
6 s	2480.7	6 a	2518.5	6 a	2556.0	6 a	2599.7		
6 s	2481.3	3 a s	c 2518.8	6 a	2556.6	6 a	2603.5		
6 a	3 s	5 a	6 s	2519.3	6 s	2557.2	6 s	2603.8	
3 s	2482.4	6 a	3 s	2520.8	6 a	2558.3	6 a	2604.4	
1 a	6 s	6 a	3 s	2521.5	6 s	2558.9	5 s	2604.9	
6 s	2483.3	1 a	2 s	2522.5	5 s	2559.6	5 s	2605.1	
3 a s	2483.7	5 a	6 s	2523.3	6 a	4 s	3 a	2605.3	
6 a	2484.7	2 a	6 s	c 2523.9	6 a	2560.3	6 s	2605.6	
6 a	2485.7	5 a	2524.7	6 a	2560.9	5 s	2606.1		
5 a	2 s	6 a	2 s	2525.1	6 a	2561.5	6 a s	2606.5	
5 a	2486.4	5 a	2 s	2526.0	6 a	2561.9	3 a s	2606.7	
5 a	2486.8	5 s	2526.7	2 a s	2562.3	6 a	2608.2		
5 a	2487.1	2 a	5 s	2527.1	2 a s	2563.2	6 a s	2608.7	
1 a	3 s	6 a	2527.9	6 a	2564.2	6 a	2609.1		
6 a	2488.7	6 a	c 2528.1	6 a	2565.1	6 s	2609.3		
4 s	2489.2	3 a	6 s	2528.9	4 s	2566.0	6 a	2610.3	
1 a	2 s	2 s	2529.2	3 a s	2566.7	6 a s	2610.7		
1 a	2 s	3 a	2529.6	5 s	2568.1	1 a s	2611.4		
2 a	2491.0	6 s	2529.9	6 a s	2568.6	6 a	2612.3		
3 s	2491.1	4 a	6 s	2530.4	6 a s	2569.4	1 a s	2613.3	
6 a s	2492.0	6 a	2531.1	5 a	2570.1	6 a	2614.0		
3 a	1 s	5 a	6 s	2532.0	4 s	2570.6	6 a	2615.0	
5 a s	2493.7	6 a	2532.4	6 s	2571.2	1 a s	2617.2		
6 a	2493.9	6 a	2532.6	6 a	2572.5	6 a	2617.6		
5 a	4 s	3 a	2 s	2533.4	6 s	2572.8	6 a	2618.3	
3 a	6 s	6 a	2 s	2534.2	6 a	3 s	4 s	2618.6	
6 a	2 s	2 a	3 s	2535.2	6 a	2574.8	5 a s	2619.9	
6 a	1 s	5 a	1 s	2536.6	5 a	2575.3	5 s	2620.4	
4 s	2500.7	3 a	2536.9	4 a	6 s	2575.7	3 a s	2621.2	
2 a	6 s	4 s	2538.0	3 a	2576.2	6 s	6 s	2622.6	
5 a	2501.4	5 a	1 s	2538.6	4 s	2576.5	3 a	6 s	2623.1
6 a	2 s	6 a	2539.1	3 a s	2577.4	6 a	2623.6		
6 a	2503.0	5 s	2540.4	6 a	2578.3	1 a s	2625.2		
3 s	2503.1	2 a	4 s	2540.8	6 a	2578.7	6 a s	2626.2	
3 s	2503.6	4 s	c 2541.6	6 s	2578.9	6 a	2626.8		
6 a s	2504.9	3 a	6 s	2541.7	6 a	2579.3	1 a s	2627.9	
6 a	2505.2	6 s	2542.4	6 a	2579.5	6 a	5 s	2629.2	
3 s	2505.8	6 a	3 s	2543.0	6 a	2579.9	6 a	5 s	2629.7
6 a	3506.2	3 a	6 s	2543.7	6 a	2580.3	1 a s	2630.7	
3 a	6 s	4 a	2544.5	6 s	2580.6	1 a s	2631.0		
3 a	6 s	5 s	2544.9	6 a	2580.9	5 a	6 s	2632.0	
6 s	2507.9	2 a	6 s	2545.8	4 a	2581.7	6 a	2632.3	
5 a	2508.5	5 a s	2546.6	4 a	3 s	2582.0	5 s	2632.9	

LIST OF ULTRA-VIOLET IRON LINES—(continued).

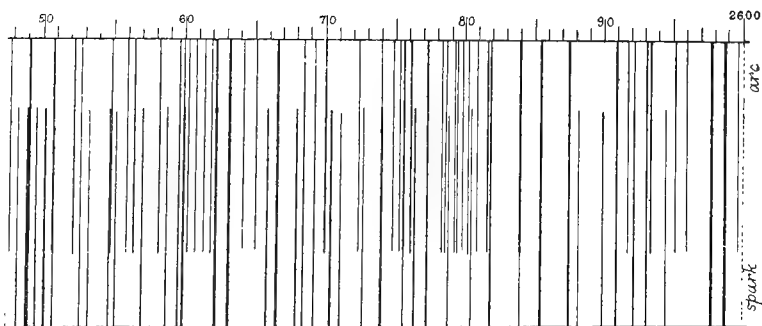
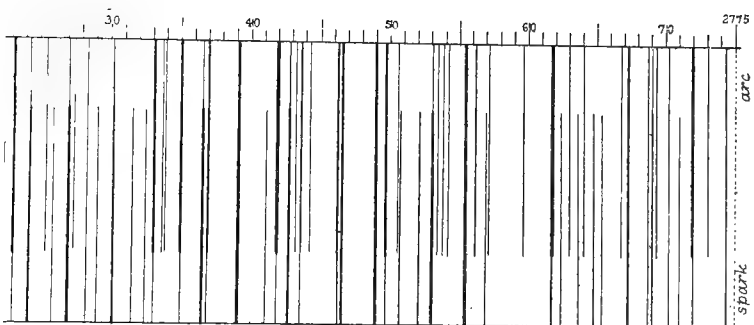
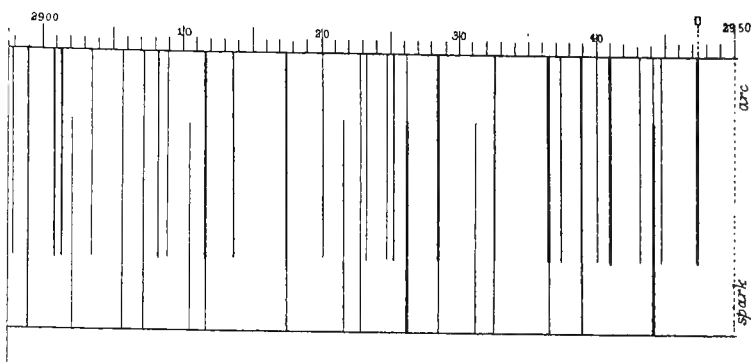
6 s	2635.1	3 a s	2688.8	6 a	2733.9	6 a	2791.5
3 a 6 s	2635.5	5 a	2689.3	3 a 5 s	2735.0	6 a	2792.2
6 a s	2636.1	5 a	2689.5	5 a 1 s	2736.5	4 s	2793.3
6 a	2636.6	6 a	2690.9	3 a 6 s	2736.9	3 a	2794.5
3 s	2637.3	6 s	2691.2	1 a s	2739.1	6 s	2796.3
4 s	2639.2	6 a	2691.7	5 s	2741.1	5 a s	2797.4
6 s	2640.7	6 a 1 s	2692.1	1 a 5 s	2742.0	3 a	2797.9
4 a	2641.4	6 s	2693.4	3 a 2 s	2742.8	6 a 4 s	2798.8
6 s	2641.7	5 a	2694.0	6 a	2743.3	6 a	2799.4
3 a 6 s	2643.8	6 a	2694.4	3 a 5 s	2743.7	6 a	2800.1
6 a 3 s	2644.9	6 s	2694.7	5 a	2744.2	3 a	2800.8
5 a	2645.2	5 a	2695.0	2 a 3 s	2746.1	6 a	2801.8
6 s	2645.8	4 a	2695.6	2 a s	2746.6	6 a s	2803.2
4 a 6 s	2647.3	6 a	2695.9	1 a s	2749.0	6 s	2803.8
4 s	2649.2	6 a	2696.6	2 a 5 s	2749.8	6 a 5 s	2804.2
6 a 5 s	2650.4	4 s	2697.0	6 a	2750.6	6 s	2804.9
6 a	2650.9	6 a	2697.7	5 s	2750.8	6 s	2805.4
6 s	2652.2	4 a 5 s	2698.6	6 s	2752.1	3 a 6 s	2806.7
6 s	2653.3	6 s	2699.8	6 a 1 s	2753.0	6 a	2807.9
6 s	2654.4	6 a 6 s	2701.2	6 a	2753.5	6 a s	2809.7
5 a s	2655.7	6 a	2702.6	6 a	2753.9	6 s	2810.9
6 a	2656.4	1 s	2703.6	6 a	2754.3	6 a	2811.7
6 a 3 s	2657.8	3 a	2705.6	1 a s	2755.5	6 s	2812.2
5 a	2660.8	1 a 3 s	2706.0	3 a	2756.2	2 a 4 s	2812.8
4 a 6 s	2661.6	6 a 4 s	2706.7	6 s	2756.9	6 s	2813.4
6 s	2662.2	3 a	2708.1	4 a	2757.2	6 a	2815.1
5 a	2663.5	4 s	2708.7	6 a	2759.7	6 a s	2817.0
6 a	2664.0	6 a s	2709.7	3 a s	2761.7	6 a s	2819.0
6 a 1 s	2664.2	4 a 6 s	2710.1	4 a	2761.9	6 a	2820.4
5 a	2665.7	3 a 4 s	2711.2	6 s	2762.4	3 a 6 s	2822.9
1 a s	2666.1	3 s	2711.5	4 a	2763.0	6 a	2823.9
6 s	2666.7	6 s	2711.9	6 s	2763.6	3 a 6 s	2825.1
6 a	2667.2	6 a	2713.5	6 a	2764.0	6 s	2827.0
6 s	2668.5	1 a s	2713.8	6 s	2764.7	6 a s	2827.3
6 a	2668.7	6 a	2714.4	6 s	2765.3	6 a 5 s	2828.3
6 s	2669.2	6 a	2714.9	6 a	2766.8	2 s	2831.0
6 s	2669.7	6 a 3 s	2715.7	3 a 1 s	2767.2	3 a 6 s	2831.8
6 a	2669.9	6 a	2717.4	6 a 4 s	2768.8	5 a	2832.4
6 s	2670.8	2 a 6 s	2718.0	6 a 4 s	2769.1	5 a	2832.8
6 a 5 s	2671.8	1 a 3 s	2718.5	6 a	2769.4	3 s	2835.2
6 a	2672.4	5 a	2719.7	6 a s	2770.3	6 s	2836.7
6 a	2674.6	1 a 4 s	2720.3	6 s	2771.1	5 a 6 s	2837.7
6 a	2675.1	6 s	2721.5	2 a 5 s	2771.9	6 a	2839.6
6 s	2676.1	6 s	2721.7	6 a	2773.1	6 a 3 s	2840.3
6 a	2677.2	5 s	2722.3	6 a 5 s	2774.5	6 a s	2843.1
2 a 6 s	2678.5	1 a 4 s	2723.1	6 s	2776.1	2 a 4 s	2843.6
6 a	2679.9	5 a 3 s	2724.3	6 s	2776.9	5 a 4 s	2845.3
5 s	2680.4	5 a	2725.5	6 s	2777.7	6 a	2846.5
6 a	2680.8	6 s	2726.0	4 a 5 s	2777.9	6 a 4 s	2848.0
6 a	2681.5	4 a 1 s	2727.1	6 a	2778.3	6 a s	2848.2
5 s	2682.0	6 a	2727.5	6 a 2 s	2778.9	6 s	2849.3
5 s	2682.4	6 a 5 s	2728.3	5 a 6 s	2781.6	6 s	2855.3
6 a	2683.5	6 s	2729.1	1 s	2783.4	6 s	2856.7
6 a 1 s	2684.2	5 a 3 s	2730.2	6 a	2784.2	4 s	2857.9
6 s	2685.7	6 s	2731.5	3 s	2785.1	6 a	2858.3
6 a	2686.0	6 s	2732.5	1 a 3 s	2788.0	6 s	2860.9
6 a	2686.8	2 a 4 s	2733.1	6 a	2789.5	6 s	2862.1
6 a	2687.3	6 a	2733.7	6 s	2790.3	6 a	2862.4

LIST OF ULTRA-VIOLET IRON LINES—(*continued*).

4 <i>a</i>	2863·1	6 <i>a</i> 5 <i>s</i>	2880·4	5 <i>a</i>	2901·3	6 <i>a</i>	2924·7
4 <i>a</i>	2863·6	6 <i>a</i> 4 <i>s</i>	2883·3	6 <i>s</i>	2902·1	6 <i>a</i>	2925·2
6 <i>s</i>	2864·7	6 <i>s</i>	2885·5	6 <i>a</i>	2903·5	6 <i>a</i> 2 <i>s</i>	2926·0
5 <i>a</i>	2866·2	6 <i>a</i>	2885·8	6 <i>a s</i>	2905·8	1 <i>a</i> 4 <i>s</i>	2928·3
6 <i>s</i>	2866·5	6 <i>a</i>	2887·3	6 <i>a s</i>	2907·1	6 <i>s</i>	2931·1
6 <i>a</i>	2867·1	6 <i>s</i>	2887·6	6 <i>a</i>	2908·2	5 <i>a</i> 6 <i>s</i>	2932·4
6 <i>a</i>	2868·0	6 <i>a</i>	2889·2	6 <i>a</i>	2908·9	1 <i>a</i> 5 <i>s</i>	2936·4
3 <i>a</i> 6 <i>s</i>	2869·0	6 <i>a</i>	2891·2	6 <i>s</i>	2910·5	5 <i>a</i>	2937·3
6 <i>s</i>	2870·7	6 <i>a</i>	2892·0	1 <i>a</i> 6 <i>s</i>	2911·5	4 <i>a</i> 6 <i>s</i>	2938·7
4 <i>a</i> 5 <i>s</i>	2872·0	6 <i>a</i>	2893·2	6 <i>a</i>	2913·6	6 <i>a</i>	2939·9
4 <i>s</i>	2873·0	5 <i>a s</i>	2894·0	5 <i>a</i> 6 <i>s</i>	2917·4	2 <i>a</i>	2940·8
3 <i>a</i>	2873·6	5 <i>a</i> 4 <i>s</i>	2894·5	6 <i>a</i>	2920·0	6 <i>a</i>	2943·1
6 <i>a</i> 5 <i>s</i>	2874·9	5 <i>s</i>	2896·7	6 <i>s</i>	2921·5	6 <i>a</i> 2 <i>s</i>	2944·0
6 <i>s</i>	2876·4	6 <i>a</i>	2897·8	6 <i>a s</i>	2922·8	6 <i>a</i>	2944·6
4 <i>a</i>	2876·8	5 <i>a</i>	2898·9	6 <i>a</i>	2923·2	U	2947·3
4 <i>a</i>	2878·2	5 <i>a</i>	2900·8				

The accompanying map is drawn to a scale double that of Ångström's and Cornu's maps of the solar spectrum. Those lines which are common to both arc and spark are drawn right across from top to bottom, while those which are in the arc only are not continued to the bottom, and those which are in the spark only do not begin at the top; so that the upper portion of the map represents the arc spectrum, the lower the spark spectrum, and they overlap in the middle.

We do not pretend to say that every line in this map really belongs to iron, for commercial iron wire was used to produce it, and the map may therefore probably include lines of a good many metals, certainly manganese lines in the arc, but it will not the less serve the purpose for which it has been made, namely: for reference in determining the approximate wavelengths of lines of any spectra.



THE ULTRA-VIOLET SPECTRA OF THE ELEMENTS.

PART II. VARIOUS ELEMENTS OTHER THAN IRON.

THE account of the ultra-violet spectra of fifteen metals here recorded is a first instalment of the results of observations which we have accumulated during the past three years, but have not heretofore been able to reduce. During that time we have taken some thousands of photographs of the electric arc under various conditions, and especially in crucibles of lime and magnesia (as previously described by us), and in the presence of most of the known metals; but with the exception of Cornu's map of the ultra-violet solar spectrum giving the chief iron lines and a few of those of other elements, up to the line U we have had little to aid us in the exploration of a new field and the assignment of the several lines to the elements producing them, and the measurement of our many photographs has cost both time and patience. Dr W. A. Miller long ago published an account of his photographs of the spark spectra of the elements, and Mr Hartley has recently (*Trans. Roy. Dublin Soc.* (2) i, p. 231) published photographs of the spark spectra of several elements which are a great improvement on those previously published. But these give spark spectra only, are taken with an apparatus of small dispersion, and are not reduced to scale, so that they give qualitative rather than quantitative results. The spectra which we here describe are those of the arc up to the wave-length 2200, and we give in each case the approximate wave-lengths of the lines observed. For some few of the lines of tin and aluminium the wave-lengths have been determined by means of a grating as described in the first part of this paper, but in all other cases they have been derived by interpolation from the wave-lengths of the neighbouring iron lines. In the map which accompanies this paper we have given in the top line the principal lines of iron for convenience of reference, and in the lowest line the arc lines of carbon with which it is necessary to be acquainted as they are always present, though varying much in intensity, in the arc taken between carbon electrodes. The scale of this map is one-half that of Ångström's "Normal Solar Spectrum."

We have already, in describing the visible spectra of the alkali metals and that of magnesium, called attention to probable harmonic relations between the lines. This relation manifests itself in three ways—first, by the repetition of similar groups of lines; secondly, by a law of sequence in distance, producing a diminishing distance between successive repetitions of the same group as they decrease in wave-length; and thirdly, a law of sequence as regards quality, an alternation of sharper and more diffuse groups, with a gradually increasing diffuseness and diminishing intensity of all the related groups as the wave-length diminishes.

The first relationship has long since been noticed in the case of the sodium lines which recur in pairs, and we have observed that the potassium lines between the extreme red and violet pairs are repetitions of a quadruple group, while the lithium lines (with the exception of the blue line mentioned below) are single, and one set of those of magnesium triplets. We now record a second harmonic* series of potassium lines which appear to be pairs, and the violet pair, and possibly the red pair too, belong to this series. Lithium shews a second harmonic series of single lines high up on the scale. Calcium gives a long series of well marked triplets; zinc likewise gives a series of triplets; aluminium gives pairs, and in the highest region triplets; thallium gives a series which seem to be quadruple groups with two of the four lines in each of much greater intensity than the rest. The alternations of sharper and more diffuse groups are generally apparent and are very marked in the cases of calcium and zinc. The diminishing distance and intensity and increasing diffuseness of successive repetitions of the same group as the wave-length diminishes, are in all the cases mentioned very plain. In all these cases the different lines forming a group are tolerably close to one another, so that successive repetitions of a group do not overlap one another, but it may be that in other cases the lines forming one group may be so far apart that the most refrangible line of one group may be more refrangible than the least refrangible line of the next repetition of the group; the groups and their sequence will thus be much less easily recognised.

Potassium.

The ultra-violet spectrum of potassium, so far as we have observed it, is apparently one harmonically related series of which the first member above the visible spectrum is a double line just below the solar line O; the next falls between Q and R, and the others follow at decreasing intervals, the seventh and last that we have observed falling just above U. It is only in the case of the line near O that we have been able to make sure that it consists of a pair of lines, but it is very probable that all are pairs in reality; all are strongly reversed, as might be expected from the volatility of the metal, and expanded when a fresh quantity of the metal or its compounds is introduced into the arc, so that the separation of the pairs, if such they be, could not be seen, while the more refrangible lines die away and are not recognisable as *bright* lines amongst the many lines which come out in the arc, as the alkali metal is dissipated. The line between Q and R, which is a strong line, happens to be in a region where the lines of iron, manganese, and chromium lie very closely, so that we cannot pronounce with certainty that it is a double line.

* By an "harmonic series" of lines we merely mean a series of overtones of a fundamental vibration; we do not mean that they follow the simple arithmetical law of an ordinary harmonic progression, but are comparable rather with the overtones of a bar or bell than with those of a uniform stretched string.

POTASSIUM LINES.

Approximate wave-length	Remarks
3445.0 } 3443.6 } 3216.5 } 3101.0 } 3033.0 } 2992.0 } 2963.4 } 2942.0 }	Double line All are easily reversed The lines become weaker as they are more refrangible

Sodium.

The sodium lines observed by us also form one apparently harmonic series with the double line, wave-length 3301, observed by Cornu. In this case also we have not been able to make out that any of the lines above 3301 are double, as when there is enough sodium present to develop them decidedly they are always more or less diffuse and reversed. Indeed, the line at 3301 is a very close pair and it is not often seen as two lines.

One line is so near to the very strong magnesium line, wave-length 2852, that the apparent development of the magnesium line by sodium was for some time an enigma to us. The sodium line is a little less refrangible than the magnesium line.

SODIUM LINES.

Approximate wave-length	Remarks
3301.0 2853.3 2679.0 2593.3	Cornu's double line All the lines are easily reversed

Lithium.

We have already described one apparently harmonic series of lithium lines extending into the ultra-violet up to about wave-length 3799. This series we described as all single lines though alternately sharp and diffuse. This description is correct, except that we have since found that one line of the series, namely, the strong blue line at wave-length 4604, is really a double line. When a fresh dose of lithium, or of some one of its compounds, is introduced into the arc, a second weaker line comes out on the more refrangible side of the strong blue line, and gives to it all the appearance of

a reversal with an expansion of the bright wings unequally extended on the two sides. As the strong blue line is, however, often really reversed, the effect is then that of a double reversal, that is to say, the appearance is that of a broad bright band with a narrower dark band within it and a bright line in the middle of the dark band. The second line rather quickly dies out as the lithium evaporates, leaving the strong blue line comparatively permanent. We have never observed any such second line, or companion, to any of the other lines of lithium. The new series begins with a line at wave-length about 3232, and dies out with a very diffuse line at about wave-length 2359. The following is a list of the ultra-violet lines we have observed.

LITHIUM LINES.

Approximate wave-length	Remarks	Approximate wave-length	Remarks
3984·5	{ Diffuse Somewhat obscured by the cyanogen bands in this region	2561·5	Reversed
3913·5		2475·0	"
3862·3		2425·5	"
3799·0		2394·5	Diffuse
3232·0		2373·5	Very diffuse
2741·0	Reversed	2359·0	Very diffuse and weak

Barium.

The barium lines are numerous, but do not fall into easily recognised harmonic series.

BARIUM LINES.

Approximate wave-length	Remarks	Approximate wave-length	Remarks
3991·8	Very strong, reversed	3320·9	(Not due to Ba) Strong Very strong Strong
3908·5		3279·8	
3891·0		3261·0	
3793·5		3070·3	
3660·7		2785·1	
3598·7		2771·0	
3592·8		2739·0	
3579·1		2702·0	
3544·0		2647·0	
3524·5		2634·5	
3499·2		2596·7	
3419·3		2542·7	
3375·6		2347·0	
3354·8		2335·0	
3347·7	(Not due to Ba)	2304·5	

Strontium.

Strontium, and its compounds, produce a line at wave-length 3705 coincident, or nearly so, with one of the lines ascribed to calcium by Cornu. We have so often observed this line much reinforced by strontium without any increase of the other calcium lines which are always present in the arc from calcium in the carbon electrodes, that we think we are justified in putting down a strontium line at this place. Two other lines of this metal are close to, but not coincident with, lines of barium.

STRONTIUM LINES.

Approximate wave-length	Remarks	Approximate wave-length	Remarks
3705·0	Coincident or nearly so with a calcium line	3458·0	Diffuse
3653·0		3379·5	
3547·0	(? not due to Sr)	3364·8	
3527·0		3305·2	
3498·0		2931·1	
3464·0			

Calcium.

Cornu has mapped two calcium lines, one on either side of the solar line M, and four other lines, of which one is coincident with the solar line R, one slightly less refrangible, and the other two more refrangible. One of these lines, at wave-length 3168·5, we have never certainly seen, but the others are well developed when calcium compounds are put into the arc. Besides these we have always seen when calcium, or one of its compounds, is present in

CALCIUM LINES.

Approximate wave-length	Remarks	Approximate wave-length	Remarks
3967·7	H	3285·0	} Sharp triplet
3972·3	} Sharp triplet	3273·5	
3956·0		3268·5	
3947·9	} K	3224·5	} Diffuse triplet
3933·0		3213·0	
3736·4	Mapped by Cornu	3208·0	
3705·5	Ditto	3181·0	Mapped by Cornu
3644·0	} Very strong	3179·0	R. Ditto
3631·0		3168·5	Ditto, not seen by us
3623·5	} Readily reversed	3158·8	Mapped by Cornu
3486·5		3151·0	} Weak, very diffuse
3474·5	} Sharp triplet	3141·0	
3468·0		3136·0	
3359·5	} Very strong	3117·5	} Weak, very diffuse
3347·5		3108·0	
3342·0		2398·0	

moderate quantity a series of triplets analogous to those of magnesium. Each triplet consists of two strong lines with a rather weaker line on their more refrangible side. This series appears to be harmonically related to the well-known blue triplet at wave-length 4454·24. The first repetition of this triplet occurs close to H, one line of the triplet falling below H, while the other two lines fall between H and K. The next triplet falls between N and M, and the next between O and N, and so on at decreasing intervals, the most refrangible repetitions becoming very faint and diffuse, so that in the last, a little below S, we have only been able to distinguish the strongest two lines of the triplet. The triplets are alternately diffuse and sharp, those near H, between O and N, and so on alternately, being the sharper. The diffuse triplets are stronger than the others and more easily reversed. Beyond this series we have noticed only one calcium line, and that is high up on the scale, at wave-length about 2398.

Zinc.

Zinc is another metal which gives a well-marked apparently harmonic series of triplets, but the different lines of each group are further separated than in the calcium or magnesium triplets. The middle line of the first triplet confounds with the sodium pair wave-length 3301, but by reason of the diffuse character of the zinc line we have not been able to decide whether the coincidence is more than approximate.

ZINC LINES.

Approximate wave-length	Remarks	Approximate wave-length	Remarks
3342·0	} Diffuse	2608·5	} Diffuse
3301·0		2582·0	
3281·0		2569·7	
3070·0		2516·0	} Very diffuse
3035·0		2491·5	
3017·0		2480·0	
2800·0		2464·5	
2770·0		2440·0	
2756·0		2430·0	
2713·3			
2684·0			
2670·5			

Mercury.

As might be expected from its volatility, it is difficult to obtain lines of mercury in the arc; but one line gives a reversed image of itself at wave-length 2536·8. This line is very bright in the flame of cyanogen, containing vapour of mercury.

Gold.

Gold also gives us but few lines. The three lines we record are perhaps harmonically related.

GOLD LINES.

Approximate wave-length	Remarks
3122·8 2675·4 2427·5	Reversed Ditto

Thallium.

Groups of thallium lines manifestly similar to one another recur, and are probably harmonically related. This recurrence is more evident in the photographs in which the lines which are expanded and reversed by the introduction of fresh metal are at once recognised. The pairs at 2921, 2710, 2609, and the lines at 2552, 2517 seem to fall into one series.

THALLIUM LINES.

Approximate wave-length	Remarks	Approximate wave-length	Remarks
3775·6		2714·6	Very diffuse
3528·3		2710·4	} Reversed
3517·8		2708·8	} Strong, diffuse, reversed
3228·1		2699·7	Very diffuse
2943·9		2665·0	Diffuse, (? not due to Tl)
2921·3		2652·3	do.
2917·8	} Very strong	2609·4	} Reversed
2895·2		2608·6	} Strong, reversed
2825·8		2552·0	Reversed
2826·9	} Single, reversed	2517·0	Diffuse

Aluminium.

The spectrum of aluminium is comparatively simple. The well-known pair of lines between H and K seem to be repeated twice in the region above without much, if any, diminution of strength, but we have not observed any such lengthened sequence of repetitions of these lines as we have of the lines of magnesium and other metals. Higher on the scale we come to another series of groups which are triplets, or perhaps quadruple groups, for the first and strongest group shews a faint fourth line which we have not observed in the succeeding groups. The repetitions we record are only two, but they lie in a part of the spectrum so near the limit of transparency of calcite that it

is quite possible that there may be more beyond, which will shew themselves when quartz prisms are used; a strong triplet near N appearing in the spark, wave-length about 3605, 3598, 3585, does not shew in the arc so far as we have observed.

ALUMINIUM LINES.

Approximate wave-length	Remarks	Approximate wave-length	Remarks
2659·8	} Strong, frequently reversed	2268·7	} Strong, diffuse
2652·0		2263·1	
2574·5		2257·3	
2567·5		2216·0	
2378·4	} A fourth faint line close to the middle line of this group. Middle line very strong, generally reversed	2210·0	(? due to Si)
2373·2		2205·0	Strong, diffuse
2366·9			Diffuse

Lead.

The lines of lead are numerous and strong, and many of them readily reversed. We have not yet traced any probably harmonic series amongst them.

Lead also gives some indefinite bands of continuous light about the region wave-length 2500.

LEAD LINES.

Approximate wave-length	Remarks	Approximate wave-length	Remarks
4019·0	} Strong, often reversed	2801·1	Often reversed
3801·0		2721·0	?
3739·3		2706·1	?
3683·3		2697·0	Middle of a very diffuse band
3670·7		2662·7	Diffuse
3639·3		2650·5	
3572·0	} " " "	2627·8	
3260·0		2613·7	Strong, often reversed
3238·6	} Nearly coincident with a line of tin	2575·7	Very diffuse
3219·6		2476·5	Strong, reversed
3118·5	} Weak lines	2446·1	" "
2981·0		2443·7	" "
2973·5		2428·5	} Very strong, reversed
2967·0		2411·5	
2872·0		2401·8	
2850·5		2399·4	
	} A little above the magnesium line, sometimes hidden by the expansion of the latter	2393·7	} Very strong, reversed
		2388·8	
2832·9	} Very strong and diffuse	2332·0	
2822·5			
	} Generally reversed		

Tin.

Tin is remarkable for the number and strength of its lines in the higher region of the spectrum, while its lines of lower refrangibility are so feeble that we have never seen any in the arc in the visible part of the spectrum. Cornu has recorded one line at wave-length 3260, and we have had no difficulty in recognising this line, but a line very nearly in that place is also developed by lead when other tin lines are not developed, and we have not been able to perceive that these lines are separable in any of our photographs. Many of the higher lines of this metal are easily reversed, indeed are almost always reversed in our photographs.

TIN LINES.

Approximate wave-length	Remarks	Approximate wave-length	Remarks
3326·0	Given by Cornu	2523·5	
3260·0		2495·5	
3175·0		2493·5	
3141·7		2483·1	
3033·0		2429·5	
3008·5		2421·5	
2986·4		2407·9	
2913·1		2392·5	
2862·8		2364·7	
2839·5		2357·7	
2813·5	(? not due to Sn)	2354·5	
2812·5		2334·3	
2787·5		2317·0	
2784·7		2286·9	
2779·5		2282·5	
2761·5		2275·4	
2660·7		2251·0	
2636·5		2245·8	
2593·5		2231·3	
2571·0		2210·7	
2557·5	(? not due to Sn)	2198·7	
2546·1		2194·1	
2530·7			
			(? not due to Sn) Strong, reversed Strong

ANTIMONY LINES.

Approximate wave-length	Remarks	Approximate wave-length	Remarks
4032·0	Close above a lead line	2597·5	} Very strong, reversed (? a single line)
3637·0		2528·0	
3265·0		2426·0	
3230·8		2383·3	
3228·0		2313·0	
3028·0		2310·0	
2876·5			

BISMUTH LINES.

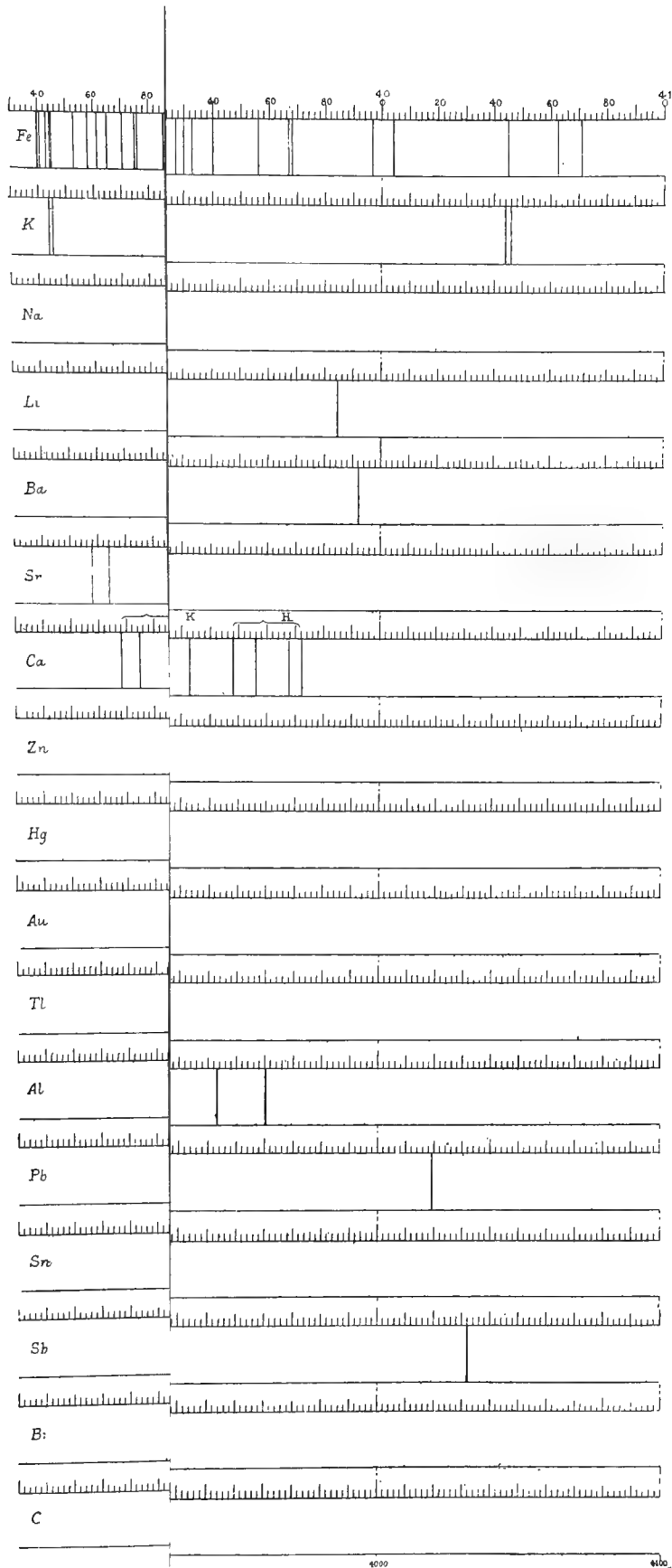
Approximate wave-length	Remarks	Approximate wave-length	Remarks
3595·3	Very strong, often reversed	2799·0	Very strong Weak, reversed
3510·4		2780·0	
3396·2		2730·0	
3066·0		2593·0	
3023·5		2524·0	
3000·0		2515·4	
2996·0		2448·0	
2937·4		2435·5	
2897·0		2431·0	
2862·0		2400·8	
2810·0		2277·0	

Silicon and Carbon.

In our map we give the silicon and carbon lines as developed in the arc. These were all attributed to carbon in the original description, but in reality are all due to silicon with the exception of the one at wave-length 2478·3 as was shewn by Hartley (*Proc. Roy. Soc.*, xxxv, p. 301). They occur in the arc taken between poles of purified graphite in air, and in nitrogen, and in carbonic acid gas, and they are always present in the arc taken in our crucibles. Most of them are also in the spark spectrum of carbon as described by us (*Supra*, pp. 178 sqq.), but some of the spark lines are not developed in the arc, and there are two lines in the arc which we did not notice in the spark.

SILICON AND CARBON LINES.

Approximate wave-length	Remarks
2881·1	Not observed in spark
2528·1	
2523·9	
2518·8	
2515·8	
2514·1	
2506·6	
2478·3	The strongest line: due to C
2434·8	
	Not observed in spark



To follow

ON AN ARRANGEMENT OF THE ELECTRIC ARC FOR THE STUDY OF THE RADIATION OF VAPOURS, TOGETHER WITH PRELIMINARY RESULTS

[*Proceedings of the Royal Society*, Vol. xxxiv. (1882), pp. 119 sqq.]

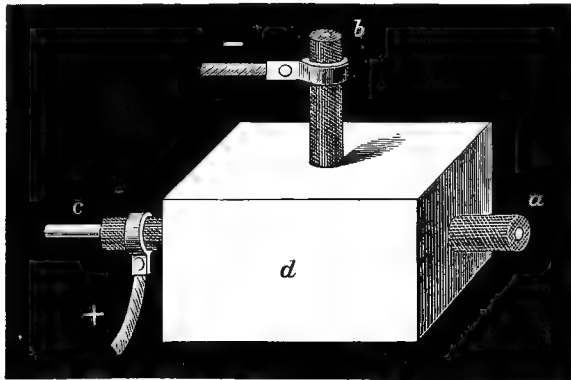
IN previous papers* we have described various devices for facilitating the study of the reversal of the lines of metallic vapour. The first series of observations were made by examining the spectrum of the interior of iron or porcelain tubes filled with vapour and heated to the highest temperature of a coke furnace, the subsequent series being visual, or photographic, records of the radiation of the electric arc surrounded by metallic vapour in the middle of blocks or tubes of lime or magnesia.

By inclosing the arc in a crucible of lime or magnesia we have found its steadiness very greatly increased, and the mass of metallic vapour which can be maintained at a temperature approaching to that of the arc much enlarged, but it cannot be said that that temperature is at all under control, and the walls of the crucible are almost always cooler than the contents. By the arrangement we have now to describe we are able to make observations through a long range of temperature, as the temperature rises and as it falls, and so to trace the influence of temperature in many cases in which the extent of that influence was before doubtful. The temperature attainable is doubtless far below that of the arc, but still it is quite sufficient to maintain iron and aluminium in the state of vapour, and shew the reversal of the lines of these elements with singular sharpness. The temperature of the interior is sufficiently high to transform the diamond into coke, even in a current of hydrogen, and the result may be taken as proving that the temperature is above that of the oxy-hydrogen flame.

The apparatus employed is thus constructed: A rod of carbon, *a* in the figure, 15 millims. in diameter, perforated down its axis with a cylindrical hole 4 millims. in diameter, is passed through a hole in a lime block *d*, and is connected by means of a copper clip with the positive electrode of a Siemens dynamo-electric machine; another carbon rod *b*, unperforated, is passed into

* *Supra*, pp. 9, 23, 25, 35.

the lime block through a second hole at right angles to the first, so that the end of the rod *b* meets the rod *a* in the middle of the block of lime. The rod *b* is connected with the negative electrode of the dynamo machine, and after contact is made between the two carbons is raised a little so that the arc discharge continues between the two carbon rods within the block of lime or magnesite. In this way the outside of the rod or tube, *a*, becomes intensely heated, the heat is retained by the jacket of lime, and the interior of the tube gradually rises in the central part to a very high temperature. By stopping the arc it can be made to pass through the same stages of temperature in the inverse order. Observations are made by looking down the perforation. When the light issuing from the tube is projected by a lens on to the slit of a spectroscope, the heated walls of the tube give at top and bottom a continuous spectrum, against which various metallic lines are seen reversed, while in the central part, when the tube is open at the farther end, the spectrum is discontinuous, and the metallic lines seen reversed against the walls at top and bottom, appear as bright lines.



By passing a small rod of carbon *c* into the perforation from the farther end, a luminous background can be obtained all across the field, and then, as the walls of the tube are hotter than the metallic vapours between them and the eye, the metallic lines are only seen reversed. A very slight alteration in the position of the carbon rod makes the lines disappear, or reappear, or shew reversal, and as the core is adjusted by eye observation before photographs are taken, all the conditions of the experiments are thoroughly known and are under easy control. We have taken photographs of the violet and lower part of the ultra-violet spectrum given by the tube at successive intervals while the temperature was rising, and noted the following results. When commercial carbons were used the first lines to be seen as the temperature rose were the potassium lines, wave-length 4044-6, next the two aluminium lines between H and K became conspicuous, then the manganese triplet about wave-length 4034, and the calcium line, wave-length

4226, then the calcium lines near M and an iron line, probably M, between them, and then gradually a multitude of lines which seem to be all the conspicuous iron lines between O and *h*. At this stage, when the small rod *c* is used to give a background, the bright continuous spectrum is crossed by a multitude of sharp dark lines, vividly recalling the general appearance of the solar spectrum. In the higher region the continuous spectrum extends beyond the solar spectrum, and the magnesium line, wave-length 2852, is a diffuse dark band, while all the strong iron lines about T, and the aluminium pair near S, are seen as dark lines. The behaviour of the calcium lines H and K is peculiar. These lines are often absent altogether, when the line wave-length 4226 and the two near M are well seen, and when the two aluminium lines between them and many of the iron lines are sharply reversed. Even the introduction of a small quantity of metallic calcium or calcium chloride into the tube did not bring them out reversed. They were only seen as bright lines, not very strong, when the small rod *c* was removed.

In some of the photographs H is visible as a bright line without K. We have formerly observed that K shews reversal in the electric arc spectrum taken in a lime crucible on the addition of aluminium, when H remains bright, and such a condition as that shewn by the hollow carbon tube where H is present without K, might legitimately have been predicted. The lithium lines at 4603 and 4131 are often bright when many other lines in the neighbourhood are reversed, and must, therefore, be regarded as relatively difficult of reversal. As a rule the lines less refrangible than 4226 are balanced as to their emissive and absorptive power, and, therefore, disappear, while the more refrangible are reversed. The cyanogen group at 3883 remain bright when the iron lines on either side are reversed; they often, however, disappear on the continuous spectrum. Many lines about P and Q of the solar spectrum are reversed. The cyanogen band above K is generally to be found in the photographs of the spectrum when only air is in the tube. It is then very faint, and is the only cyanogen group visible. If ammonia is passed into the tube the fine set above K, the N group, and, although less plainly marked, the set at 4218, appear. In one plate the three lines at 4380 and the group of seven at 4600 appear along with the blue hydrocarbon set. It is well known that ammonia reacts on carbon at a white heat, producing cyanide of ammonium and hydrogen, so that the genesis of the cyanogen spectrum under the present conditions is a crucial test of the validity of our former observations on this subject, which are, however, in marked disagreement with the results obtained by Mr Lockyer, in his review of the same field of investigation.

Both the indium lines 4101 and 4509 are persistently reversed, together with several lead lines. Tin gives flutings in highly refrangible portions of the spectrum, and silver gives a fine fluted-looking spectrum in the blue.

Chloride of calcium gives a striking set of six or seven bands between L and M, which may be seen both bright and reversed.

When the small rod *c* is removed, it is easy at any moment to sweep out the vapours in the tube by blowing through it; it is equally easy to pass in reducing or other gases. Ammonia introduced seems to facilitate the appearance of reversed lines. On passing this gas through a tube containing magnesia, the set of lines just below *b*, which we have always found to be associated with the presence of magnesium and hydrogen, and is most probably due to some compound, instantly appear.

The above is a brief abstract of the few observations we have been able to make as a preliminary to a more thorough research, and we feel warranted in thinking that the method promises to solve some intricate spectroscopic problems. When we can command several electric arcs to heat a considerable length of carbon tube, and are enabled to examine the radiation of a powerful arc passing through vapours in the tube, valuable results may be anticipated.

GENERAL OBSERVATIONS ON THE SPECTRA OF CARBON
AND ITS COMPOUNDS

[*Proceedings of the Royal Society*, Vol. xxxiv. (1882), pp. 123 sqq.]

IN our former two papers on the spectra of the compounds of carbon with hydrogen and nitrogen (*Supra*, pp. 85, 100) we described the results of a long series of synthetical and analytical experiments which had enabled us to trace satisfactorily a fluted band spectrum which occurs in the arc and spark discharge in many compounds of carbon, and generally when carbon poles are used to transmit the current of the arc or spark in air, to the compound substance cyanogen. This led to a further investigation of the carbon ultra-violet line spectrum in order to complete the series of simple vibrations which originate from this substance. After all this work a great deal remains to be ascertained regarding the conditions which cause a variation of intensity in the different series of carbon flutings which originate from cyanogen, and also their persistency and development.

The present paper is a short record of the particular variations in the carbon groups which are revealed in the different photographs of the spectrum of the arc discharge that we have had occasion to take for other purposes, together with some new observations on the genesis of the cyanogen spectrum during combustion.

The remarkable discovery of Dr Huggins, regarding the occurrence of two of the most marked series of cyanogen bands in last year's comet, adds considerable interest to this question, and has induced us to make a further study of the chemical reactions in flames which cause this particular spectrum to appear at a relatively low temperature.

Electric Discharge between Carbon Poles in different Gases.

In order to facilitate reference the general appearance of the portion of the cyanogen spectrum to which we shall refer is given in the diagram overleaf.

The apparatus used in the experiments has been already described in our papers on the spectra of the compounds of carbon with hydrogen and

nitrogen (*Supra*, pp. 88, 108). No attempt was made to use perfectly pure gases or to remove all traces of nitrogen from the vessels employed: the object being to study the variation of the groups of lines, perfect purity in the gases was not required.

The arc discharge between graphite poles in carbonic acid shews the triple set, beginning about 4380, with traces of the other sets of cyanogen bands at 4218 and 3883. If the carbonic acid gas is displaced by air, the triple set are very much weakened and are sometimes invisible, while the other fluted series at 4218 and 3883 are greatly strengthened.

The spark discharge does not shew the cyanogen sets in carbonic acid, but a series of five groups appear between the limits of the lines S and N of the solar spectrum, which may possibly be due to carbonic acid or carbonic oxide. The carbonic oxide flame, however, does not shew this set. If the spark discharge is taken between graphite poles in nitrogen all the cyanogen series appear; but in hydrogen they sometimes disappear. As a rule, however, they remain faint even when a current of the gas is kept continuously passing through the bulb in which the discharge is taken. With the arc discharge in hydrogen the triple set are well marked, while the series at 4218 disappear, and the ultra-violet group are just visible; the hydrocarbon band, however, at 4310 comes out strong.

In order to ascertain how the pressure of the surrounding atmosphere affected the emissive power of the cyanogen produced synthetically in the arc discharge, a series of observations on the spectra obtained under diminished pressure of the gaseous atmosphere was undertaken. The pressure in different gases was reduced to a mean value of about 1 inch of mercury, and under such conditions the intermittent discharge of the De Meritens machine was examined. The arc in air, under these circumstances, shewed the blue hydrocarbon set; all the cyanogen series of bands together with a nitrogen series near H. Carbonic acid at the same pressure had the triple set of lines strongly marked, while the others were decidedly weaker, as in the experiments with the gas at atmospheric pressure.

In hydrogen, at equal pressure, the triple set disappear, and the hydrocarbon band at 4310 occurs, which is not generally seen in the photographs of the arc spectrum. But what is very remarkable is the appearance of two



lines of carbon, viz., 2836·3 and 2837·2 (also 2506 of Si and 2508 of C) in the spectrum of the discharge, whereas these spark lines are not generally found in the arc spectrum.

The following lines of silicon*, and one of carbon, have been observed in the arc discharge of the Siemens continuous current machine, as well as in that of the De Meritens intermittent current, taken in air. We have observed in previous experiments that the De Meritens arc in hydrogen produces a sufficient temperature to render the C line of hydrogen permanently visible. The continuous Siemens current, under the same circumstances, only shews this line when the arc is produced by breaking the contact of the poles, not with the steady arc.

Approximate Wave-lengths of Silicon and Carbon Arc-lines.

2434·8 absent from spark.

2478·3 strongest line. Due to C.

2506·6.

2514·1.

2515·8.

2518·8.

2523·9.

2528·1.

2881·1 not in spark.

We have here another instance of the lines of high refrangibility appearing, under certain circumstances, when no trace of strong lines belonging to the less refrangible portion of the spectrum can be detected. Thus the strong carbon line in the blue at 4266 does not appear in the photographs of the arc spectra. Of course it is possible that a very long exposure of the photographic plate might reveal some of the missing lines, as we have shewn in other cases. The presence of these carbon lines is a proof that carbon vapour of a definite, but probably low, tension exists in the arc discharge, and this is doubtless the reason why under such conditions carbon combines with hydrogen and nitrogen with such facility. By a careful series of experiments carried out at different pressures with varying electric power we hope to ascertain with greater precision the variations in the carbon line spectrum.

Eye Observation of Spectra.

When the spectrum of different parts of a magnified image of the electric arc is examined, all the more refrangible cyanogen groups may be seen near the positive pole, together with a series of channellings in the red. When the arc is steady the cyanogen spectrum is permanently visible at the

* See above, p. 230.

negative pole, when no trace of the hydrocarbon series can be seen. In the same way the arc in the middle of a magnesia crucible often shews no trace of the hydrocarbon set, although the cyanogen bands are strong. If, however, puffs of air or carbonic acid are passed into the arc, the hydrocarbon lines are produced. There is always, under these circumstances, far greater variation in the brightness of the hydrocarbon series than of the cyanogen, in fact, the presence of magnesia rather favours the steady formation of cyanogen. When the hydrocarbon spectrum is strong the brilliancy and number of the cyanogen groups that are visible are undoubtedly increased, so that the one variety of vibrations seems to affect the other. This is easily accounted for by the chemical interaction which takes place between acetylene, nitrogen, and hydrocyanic acid. The hydrocarbon spectrum is brought out at once in the magnesia crucibles by moistening one of the poles. All such actions seem to shew that hydrogen is essentially connected with the production of this fluted spectrum just as nitrogen is with the cyanogen series.

Arc Discharge in Fluids.

The De Meritens arc, taken in water, shews the hydrocarbon spectrum alone; no cyanogen bands can be seen by eye observation, even when ammonia or nitrate of potash is added to the water. In this case the observations are rendered uncertain from the great intensity of the continuous spectrum. If glycerine is used instead of water no cyanogen groups of lines can be recognised, but on adding a little nitrobenzol the set of three lines (about 4380) peculiar to the cyanogen spectrum appear, this being the only group which can be detected by the eye on the continuous background. This result supports the observations on the varying intensity of this group in different gaseous media, and seems to shew that conditions can be found where it is the most characteristic group of cyanogen. These three lines are easily seen in the spectrum of the arc taken in carbonic acid, although they disappear from the spectrum of the arc taken in air.

Vacuum Tube Spectra.

In our former experiments with vacuum tubes we did not use a capillary glass tube, but preferred to examine the photographic spectrum obtained from a short spark taken between platinum wires. Objection has been taken to this plan of working on the ground that, as the capillary form of vacuum tube increases the brilliancy of the spectrum, particular lines or groups of the spectrum which otherwise would be missed, might be revealed in them, and such tubes ought, therefore, to have been employed. In order to answer this objection we have prepared and examined vacuum tubes of this kind containing benzol and benzol with naphthalene in solution, using all the precautions to avoid the presence of nitrogen formerly described, and have always found such tubes free from any trace of the cyanogen spectrum. When such tubes are,

however, examined daily, the cyanogen bands often appear after a time, and this can be traced in all such cases to a leak or crack at the point where the platinum is sealed into the glass. No perfectly pure hydrocarbon gives the series of bands we attribute to cyanogen*.

Observations on Flames.

The temperature produced by the combustion of hydrocarbons and other non-nitrogenous organic bodies well supplied with oxygen, is not sufficient to induce the combination of nitrogen with carbon, so that the cyanogen spectrum is absent from such flames. We know, however, that hydrocyanic acid is often produced in the oxidation of organic bodies containing nitrogen, and that ammonia reacts with carbon at a white heat, producing hydrocyanic acid and hydrogen. Such actions led us to expect that the cyanogen spectrum ought to appear in the flames of organic compounds containing nitrogen, provided the temperature were sufficient to render the radiation of this substance sufficiently intense. Our first experiments did not succeed. The most careful examination by the eye of the spectrum of a hydrogen flame which had passed through a solution of hydrocyanic acid or of a flame of alcohol containing nitrobenzol or nitrite of ethyl, did not result in any recognition of the strong cyanogen groups. This failure led to a chemical examination of the composition of the gases withdrawn from the interior of such flames, in order to ascertain the combustible mixtures which react during combustion to produce hydrocyanic acid. The gases were extracted from the flame with an apparatus similar in principle to that employed by Deville in his *Chemical Researches on Flame*. When coal gas is passed through a solution of ammonia and burnt, the flame gases contain hydrocyanic acid and acetylene, but if oxygen is well supplied to the flame no cyanogen reaction is given by the extracted gas. Carbonic oxide mixed with ammonia in the same way gave no trace of hydrocyanic acid during combustion: even when a large quantity of the mixture was burnt and the flame gases continuously withdrawn no appreciable cyanogen reaction could be detected. Similarly hydrogen mixed with a little carbonic acid and ammonia gave no cyanogen reaction. When hydrogen is passed through ammonia solution mixed with chloroform, tetrachloride of carbon, bisulphide of carbon, or picoline, cyanogen can always be recognised in the flame gases. Chloroform under such circumstances yields the largest amount. When a mixture of

* It is worthy of note that the strong carbon line wave-length 2478.3 present in both the arc discharge and in the spark discharge in carbon compounds at atmospheric pressure, is not found in the spectrum of the spark in cyanogen at low pressure. We have tried to obtain a photograph of it from a "Plücker" tube fitted with a quartz end, and placed end-on in front of the spectro-scope, but found no trace of it. As this line appears in the spectrum of the flame of cyanogen, its absence from the spark discharge in cyanogen of low tension seems intelligible only on the supposition that the discharge is selective in its course, and lights up only certain of the substances present; or else that the quantity of carbon vapour present at any instant is so minute, as to produce no sensible effect on the photographic plate.—July 10, 1882.

carbonic oxide and ammonia is passed through a porcelain tube heated in a furnace, large quantities of hydrocyanic acid are produced, especially when the moist gases are employed. Ammonia passed over perfectly pure graphite at a white heat produces hydrocyanic acid, and the vapour of chloride of ammonium is equally efficient in bringing about this reaction. It appears to result from the experiments that hydrocyanic acid can always be separated from the interior of flames such as we have employed, provided that portion of the flame which, in carbon compounds, is characterised as reducing, be selected. That stage of combustion during which free carbon or dense hydrocarbon vapours containing very little hydrogen are formed, is favourable to the formation of hydrocyanic acid, as ammonia can at this stage react on the carbon. It is quite possible, however, that hydrocyanic acid may exist in small quantity in some of the flames which tested according to this method appear to contain none, and that notion is favoured by the consideration of the dissociation phenomena which are known to occur in flames. This led us again to spectroscopic examination as the most delicate test for the presence of cyanogen, but instead of trusting to the eye as in former experiments, photographs were taken of the spectra of flames by means of a quartz and calspar train, and the exposure of the plate purposely prolonged. Thus examined, it was found that coal gas well supplied with oxygen gave only the hydrocarbon groups, together with the two interesting additional lines first discovered by Dr Huggins, having the wave-lengths 3872 and 3890; but when the coal gas passed through ammonia the photographs revealed the characteristic cyanogen groups at 3883 and 4218, the most refrangible group being the strongest. The cyanogen spectrum can then be produced synthetically from nitrogen compounds in flames along with the hydrocarbon spectrum, so that the appearance of the groups of cyanogen is not always associated with a very high temperature such as we have in the electric arc. Cyanogen once formed gives its peculiar spectrum at the relatively low flame temperature produced by burning cyanogen mixed with carbonic acid. Of course the mean temperature of a flame is very different from the temperature of individual molecules, and this complicates the problem we are discussing. The thermal equivalents of cyanogen and acetylene being highly negative, it is certain that these substances yield on combustion the highest temperature of any two compounds burning in oxygen; and we have shewn in a former paper that burning cyanogen in nitric oxide gas, which probably induces a still higher temperature, does not bring about any marked change in the character of the spectrum. Spectroscopic analysis can thus detect very small quantities of cyanogen under widely different physical conditions. As the temperature of the flame of cyanogen probably approaches the temperature of the carbon poles of the electric arc, and as we have shewn that carbon undoubtedly exists in the form of vapour in the arc discharge, from the fact of the ultra-violet line spectrum being present, the question naturally arises,

is carbon present in the form of vapour in the cyanogen flame? In order to answer this question we have taken photographs of the ultra-violet spectrum of the cyanogen flame fed with oxygen, and with long exposures have had no difficulty in detecting one of the strongest carbon lines, viz., that at 2478·3, along with a trace of what may be the pair of lines at 2837, but more probably is a mercury line. No other carbon line was found in the photographs. It seems, therefore, proved that carbon vapour does exist in the flame of cyanogen, although to a much smaller extent than in the arc discharge. Observations must be made on the spectra of flames under high pressures, in order to solve many problems connected with spectroscopic enquiry, and this subject we hope to discuss in a future communication.

NOTE ON THE REVERSAL OF THE SPECTRUM OF
CYANOGEN

[*Proceedings of the Royal Society*, Vol. XXXIII. (1881), pp. 3 sqq.]

IN the course of many observations on the reversal of lines of metallic spectra, we have frequently noticed dark shaded bands which appeared to be the reversals of bands ascribed to the oxides or chlorides of sundry metals; more particularly we have seen them when experimenting with compounds of the alkaline earths, and we have repeatedly obtained a reversal of the green magnesium-hydrogen series; but, until recently, we have never seen any reversal of the shaded bands of the spectrum of cyanogen, though our attention has been constantly directed to this spectrum. Quite lately, however, we have obtained photographs which shew the reversal of the violet and ultra-violet bands of this spectrum; and the fact is perhaps of sufficient interest, especially in connexion with the question of the occurrence of these bands amongst the Fraunhofer lines, to warrant the publication of this note. We have not yet succeeded in determining precisely the conditions under which the reversal can be produced at will. The most complete reversals of these bands were obtained by the use of the arc of a Siemens machine, in a crucible of magnesia, fed with a considerable quantity of cyanide of titanium. The photographs in this case shew a very complete reversal of the five bands near L, and of the two strong bands near N, and a less complete reversal of the six bands, beginning at about wave-length 4215. No other metallic cyanides have given, when introduced into the crucible, any such reversal; nor does a stream of cyanogen led in through a perforated carbon produce the effect. Various other nitrogenous compounds have been tried, but the only one which has given us anything like the effect of the titanous cyanide is borate of ammonia. Some photographs taken immediately after the introduction of borate of ammonia shew distinctly the reversal of the group of bands near L. In one case when metallic magnesium had been put into the crucible, the photograph shews a reversal of only that part of the series which is nearest to the magnesium group, indicating that the reversal is due to the

bright background supplied by the expanded magnesium lines. There can be little doubt that the greater stability of titanic cyanide and boron nitride than of other nitrogenous compounds, has some influence upon the result; and the difficulty in producing the reversal at will is in securing an absorbent stratum of sufficiently high temperature and at the same time a sufficiently luminous background. The circumstances which secure the former condition almost always produce in the arc a still more intense radiation of just those rays which are absorbed, without that expansion of the lines which shews out the absorption in the case of so many metallic spectra. The photographs are, however, conclusive evidence that it is possible to secure both conditions.

ON THE CIRCUMSTANCES PRODUCING THE REVERSAL OF SPECTRAL LINES OF METALS

[*Proceedings of the Cambridge Philosophical Society*, Vol. iv. Pt. v.
(1882), pp. 256 sqq.]

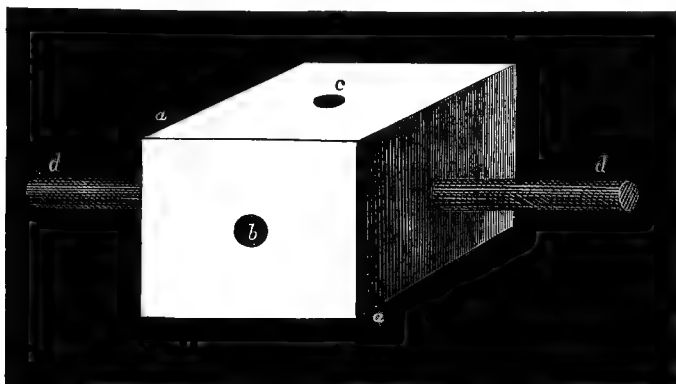
OUR object in investigating the reversals of the lines of terrestrial elements has been to trace the parallel between the conditions of the elements as they exist in the sun, and those in which we can place them on earth; with a view to illustrate more fully the problems of solar chemistry. A knowledge of the reversible lines may also help us to distinguish those rays which are directly due to the vibrations communicated to the luminiferous ether by the freely moving molecules themselves from those which are produced by superposition of waves, or by some peculiarity in the mode in which the molecules are put in motion, or by some strain upon them, such as the violent Leyden jar discharge might give, which would not be an easily reversible action.

In a former communication* we brought before the Society the results of our observation of the reversal of the lines of some of the more volatile metals when the continuous spectrum of the hot walls or end of an iron or porcelain tube was observed through vapour filling the tube. As the temperature of the tubes was only that of a crucible furnace (about 1500° C. at the highest), it was a very limited number of the lines even of the volatile metals which could be reversed in that way, because the relative strength of the emissive (and therefore of the absorptive) power of a vapour for particular rays often varies considerably when the temperature is changed. Thus the vapour of sodium in an ordinary flame emits little radiation except that of the yellow pair of lines and only absorbs the same; and it is only at higher temperatures such as that of the electric arc, or that of a flame locally increased by the introduction of an endothermic salt such as a chlorate, that the other pairs (or groups) of lines red, orange, green and blue are seen either bright or reversed. We want then a source of light which shall give a more or less continuous spectrum of an intensity greater than that of the lines to be observed, and the metallic vapour not only in a layer of some thickness but heated up till it is capable of freely emitting the light of those lines

* *Supra*, p. 3.

which we want to reverse. In the case of the less volatile metals such as iron and aluminium it would not be expected that these conditions should very easily be fulfilled.

After trying the oxy-hydrogen jet to ignite the bottom of a tube bored in a block of lime, which gave us reversals of the well-known green and orange bands of lime, and of the blue line of calcium which was barely reversible in tubes heated in a crucible furnace, we turned our attention to the electric arc as a source of heat both to give the requisite bright background and to vaporize the metals examined, but enclosed it in a block of lime or magnesia, by which we were able to maintain a considerable amount of refractory metal in a state of vapour, and from the tube-like form of the opening through



- a.* Block of lime or magnesia.
- b.* Hole bored to the centre of block through which observations were made of the arc.
- c.* Hole by which metals were dropped into the arc, usually covered with a piece of lime.
- d, d.* Carbon rods forming electrodes of dynamo-electric machine.

which the arc was viewed could observe the absorption of a tolerable thickness of such vapour gradually diminishing in temperature as it receded from the arc. The greater part of our observations were made with some one or other of several modifications of this apparatus.

For the ultra-violet part of the spectrum photography was used. Generally 15 photographs were taken on the same plate in order to vary the time of exposure, as good impressions of faint lines cannot be obtained without over exposing the strong lines: and also in order to catch different phases of effect as the metal introduced evaporates.

The reversals thus observed may be classed under several heads.

I. Reversals by the expansion of the line observed, or, as they may be called, self-reversals. These are the reversals most generally known. The

sodium lines are frequently so reversed, indeed always when a sufficiently volatile salt of sodium such as the carbonate or chloride is held in a gas flame. If sufficient sodium is in the flame the lines are widened, and the less dense and less hot sodium vapour outside the flame produces a narrow absorption line down the middle of the bright yellow band. In this way the metal itself gives the background against which the reversed line is seen; and in order to produce the result the line must be more expanded at the higher temperature than at the lower. That does not always happen, but it is so frequent that many reversals may be seen in this way. The magnesium line of wave-length 2852 has great power of expansion and is always seen reversed in this way when the arc is taken in a magnesia crucible as in Plate I. fig. 1.

One set of the photographs exhibited are original negatives of the arc spectrum shewing reversals of this class in the case of lines of magnesium, thallium, indium, tin, aluminium, antimony, lead and zinc. They are only a selection out of a very large number taken by us but sufficient to shew the characters of this class of reversals.

Professor Hartley has lately (*Proc. Roy. Soc.* xxxiv. 84) called attention to the pseudo-reversals of this class which may be produced in the case of a strong line by over-exposure. It is well known that over-exposure (solarization as we used to call it formerly) produces such an alteration in the sensitive preparation of the photographic plate that the over-exposed parts cease to be developable, so that a very strong line may appear white in the negative where it ought to be black, but with a dark border, and so give the appearance of a reversed line. Professor Hartley finds it difficult to distinguish real reversals of the class we are now discussing from these pseudo-reversals. His difficulty has not occurred to us, first because we have always been in the habit of taking our photographs in series with varying exposure, in order to get impressions both of the feeble lines in some and of strong lines in others; and secondly because we almost always close part of the slit of the spectroscope with a shutter so that the image is cut off sharply by the shadow of the shutter. Strong lines extend into the shadow more or less, and if there is a real reversal the extension of the reversed part into the shadow is trumpet-shaped (*a*), whereas if it is only a pseudo-reversal it is closed (*b*).



We would call especial attention to the enormous expansibility of the magnesium line w. l. 2852. The limits are quite indefinable either up or down the spectrum and the absorption (*i.e.* the reversed line) is a broad band, sometimes reaching up to the solar line U as seen in Plate I. fig. 2, which is a negative photograph of the same part of the arc as fig. 1, but had a fragment

of magnesium dropped into it at the moment it was taken. You might fancy that magnesium were the substance which produces the absorption of the sun's rays above U, if it were not that the light reappears in the case of magnesium above the dark band as well as below it while the sun's light seems to be quite cut off above U. The cessation of the solar spectrum above the magnesium line may be due to the general absorption of the lines of iron and other metals which are far more numerous in that region than in the visible part of the spectrum, and it is just possible that a very long exposure of sensitive plates may yet reveal some extension of the solar spectrum beyond U.

In these cases of self-reversals the light of the line is only partially absorbed, but there are other cases:

II. Complete reversals, where the lines are seen only as dark lines. To this class belong the reversals before described when the lines of volatile metals were seen dark against the bright background of the hot bottom and sides of the tubes heated in a furnace. But the arc itself does not generally give such a background. It gives generally a discontinuous spectrum consisting of bright lines with only a very faint continuous spectrum. There are however some parts of the arc, as we used it, which are so full of fine closely set lines that it serves as a good background against which a dark reversed line can be seen. The tail of fine lines formed by the ultra-violet cyanogen bands is such a region. Another is in the neighbourhood of Q where there are a great many fine iron, manganese and chromium lines, and where also the fine lines of the water spectrum add to the effect so as to give something like a continuous spectrum.

One of our photographs shews the reversal of a thallium line near L. In the negative photograph it is a simple absorption line. Another photograph shews silver lines near Q reversed as mere white lines on the general spectrum. In some cases we have succeeded in getting a good background by bringing up the hot carbon pole into the line of view. In that case the larger part of the bright metallic lines disappear and the continuous spectrum becomes much stronger, so that the reversed lines are more readily seen. We have various plates shewing complete reversals of the lines of several metals in one or other of these ways. The ultra-violet lines of potassium form a series extending at decreasing intervals to about the solar line U. They are all reversed, appearing only as white lines in the (negative) plates. The least refrangible is a double line just below O. Probably they are all double in reality, and harmonically related to the violet pair. Plate II. shews most of these potassium lines reversed.

In other plates are seen complete reversals of copper and silver, and lead lines. Some of our plates shew complete reversals of a great many iron

lines. In two of these plates the reversals were obtained by putting an iron wire into the arc through one of the carbons, which was perforated for the purpose. Some of the lines are greatly expanded, but they appear only as absorption lines; they have no bright wings. In another case the iron was introduced into the arc as ferrocyanide of potassium, and the lines are sharp clean fine lines just like the Fraunhofer lines in the solar spectrum, the bright continuous background being heightened by the potassium, which seems to give some continuous spectrum in the ultra-violet region. Plate III. shews a great many iron lines so reversed.

III. Another class of reversals are produced by the vapour of one metal seen against a bright background given by the expansion of a bright line of some other metal. For this purpose the expanded lines of magnesium are most effective from their great breadth. We have several plates shewing sharp clean reversals of iron lines against the continuous light of the expanded magnesium line, w. l. 2852; one shews lines reversed in this way against the bright expansions on both sides of the absorption band of magnesium. One of the plates shews some iron lines near M and chromium lines reversed in this way. Plate I. fig. 2 shews the principal iron lines between S and U reversed against the expanded magnesium line w. l. 2852.

IV. A fourth mode of obtaining reversals we cannot so easily explain. It is by allowing a very gentle stream of hydrogen, coal gas, or ammonia, to pass into the arc either through one of the carbons perforated or through a separate opening into the crucible. The effect of such a current is generally to sweep away most of the metallic lines, make those which remain fainter, and increase, relatively at least, the continuous spectrum, and reverse many lines. The character of the effect is fairly seen in a photograph, Plate IV., of the part of the spectrum near U, in which the magnesium line (2852) appears about as strong as usual in a magnesia crucible, but wholly as an absorption, while the other magnesium lines are still bright. Many of the iron lines are reversed in this photograph, and so are some less refrangible calcium lines. No doubt many of the other lines which have disappeared are not seen because absorption just balances emission. Indeed by varying the current different effects may sometimes be produced, the same line appearing at one time bright, at another time dark, and at another time not at all. We have seen the calcium lines at H and K, and the strong blue triplet just below the well-known (indigo) calcium line at wave-length 4226 all bright, while the indigo line itself was quite invisible, it was neither bright nor reversed. This and similar effects are no doubt due to differences in emissive power at the different temperatures of the emitting and absorbing vapour. At the higher temperature the emissive power of calcium for H and K and the blue triplet is relatively greater than for the indigo line, while

at the lower temperature of the absorbent vapour the reverse holds; so that the emission for the indigo light is balanced by absorption, while that of the other rays is not balanced. In like manner we have frequently seen H when K was quite invisible, sometimes K reversed when H was not reversed.

It is not at first sight easy to explain the action of the gas. Probably hydrogen is the chief agent in the case, for a mere current of air has no such effect. The gas may act by helping to diffuse the metallic vapours, diminishing their density in the arc, and increasing it in the tubular part of the crucible without too much lowering the temperature. Hydrogen gas also maintains a reducing atmosphere, preventing the oxidation of the metallic vapour. It also forms compounds with some metals, notably with magnesium and the alkali metals, as well as with the carbon of the electrodes, which are probably all endothermic, and whether that be so or no, must affect the distribution of the temperature in the arc and tube. In the case of expanded bright lines, when they are not wholly swept out by the gas the effect is to diminish the wings, and as absorption does not begin at the wings, this can only be by diminishing the range of emission, probably by diluting the metallic vapour. The amount of heat absorbed by such a small mass of gas will not lower the temperature much. Moreover a current of chlorine has usually the opposite effect to that of a current of hydrogen, increasing the strength of the bright lines, probably by assisting the volatility of the metals, and so increasing the quantity in the arc. That the explanation here offered of the action of hydrogen is correct, is borne out by the behaviour of mixtures of metals. Thus an alloy of zinc with a little lead gives far sharper and cleaner reversals of the lead lines than lead alone does. When lead alone is put into the arc in the crucible the lead lines come out very strong and diffuse, and the emission is not nearly balanced by the absorption in the (comparatively) cool tube; but when the alloy with zinc is used the lead lines are much less expanded and the emission much more nearly balanced by the absorption.

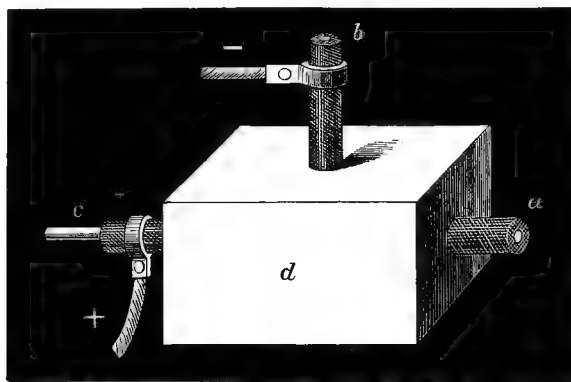
By inclosing the arc in a block of lime or magnesia we have found its steadiness very greatly increased, and the mass of metallic vapour which can be maintained at a temperature approaching to that of the arc much enlarged, but it cannot be said that that temperature is at all under control, and the walls of the crucible are almost always cooler than the contents.

V. We have lately used a carbon tube, passed quite through a block of lime, and made it the positive electrode of the current, while the other electrode is a carbon rod passed into the lime at right angles to the tube so as to meet it in the middle.

In this way the outside of the tube becomes intensely heated, the heat is retained by the jacket of lime, and the interior of the tube gradually rises in

temperature and attains in the central part a very high point. By stopping the arc it can be made to pass through the same stages of temperature in the inverse order. Observations are made by looking down the perforation. When the light issuing from the tube is projected by a lens on to the slit of a spectroscope, the heated walls of the tube give at top and bottom a continuous spectrum, against which various metallic lines are seen reversed, while in the central part, when the tube is open at the farther end, the spectrum is discontinuous, and the metallic lines seen reversed against the walls at top and bottom appear as bright lines. Plate V. is a negative photograph shewing this effect.

The apparatus employed is thus constructed: A rod of carbon, *a* in the figure, 15 millims. in diameter, perforated down its axis with a cylindrical hole 4 millims. in diameter, is passed through a hole in a lime block *d*, and is connected by means of a copper clip with the positive electrode of a Siemens dynamo-electric machine; another carbon rod *b*, unperforated, is passed into the lime block through a second hole at right angles to the first, so that the end of the rod *b* meets the rod *a* in the middle of the block of lime. The rod *b* is connected with the negative electrode of the dynamo machine, and after contact is made between the two carbons is raised a little so that the arc discharge continues between the two carbon rods within the block of lime.



By passing a small rod of carbon into the perforation from the farther end, a luminous background can be obtained all across the field, and then, as the walls of the tube are hotter than the metallic vapours between them and the eye, the metallic lines are only seen reversed. A very slight alteration in the position of the small carbon rod forming a core to the tube makes the lines disappear, or reappear, or shew reversal, and as the core is adjusted by eye observation before photographs are taken, all the conditions of the experiments are known and are under easy control.

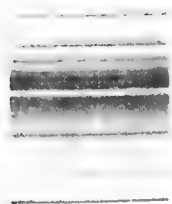
By this arrangement we are able to make observations as the temperature rises and as it falls, and so to trace the influence of temperature in many cases in which the extent of that influence was before doubtful. The temperature attainable is doubtless far below that of the arc, but still it is quite sufficient to maintain iron and aluminium in the state of vapour, and shew the reversal of the lines of these elements with singular sharpness. The temperature of the interior is sufficiently high to transform the diamond into coke, even in a current of hydrogen, and the result may be taken as proving that the temperature is above that of the oxy-hydrogen flame. We have taken photographs of the violet and lower part of the ultra-violet spectrum given by the tube at successive intervals while the temperature was rising, and noted the following results. When commercial carbons were used, which always contain iron, aluminium, manganese, calcium and magnesium as well as traces of other metals, the first lines to be seen as the temperature rose were the potassium lines, wave-length 4044-6, next the two aluminium lines between H and K became conspicuous, then the manganese triplet about wave-length 4034, and the calcium line, wave-length 4226, then the calcium lines near M and an iron line, probably M, between them, and then gradually a multitude of lines which seem to be all the conspicuous iron lines between O and *h*. At this stage, when the core is inserted to give a background, the bright continuous spectrum is crossed by a multitude of sharp dark lines, vividly recalling the general appearance of the solar spectrum. In the higher region the continuous spectrum extends beyond the solar spectrum, and the magnesium line, wave-length 2852, is a diffuse dark band, while all the strong iron lines about T, and the aluminium pair near S, are seen as reversed lines. The behaviour of the calcium lines H and K is peculiar. These lines are often absent altogether, when the line wave-length 4226 and the two near M are well seen, and when the two aluminium lines between them and many of the iron lines are sharply reversed. Even the introduction of a small quantity of metallic calcium or calcium chloride into the tube did not bring them out reversed. They were only seen as bright lines, not very strong, when the small rod was removed. The lithium lines at 4603 and 4131 are often bright when many other lines in the neighbourhood are reversed, and must therefore be regarded as relatively difficult of reversal. As a rule the lines less refrangible than 4226 are balanced as to their emissive and absorptive power and, therefore, disappear, while the more refrangible are reversed.

Both the indium lines 4101 and 4509 are persistently reversed, and so are several lead lines. Tin gives lines, of which some are reversed, in highly refrangible regions besides a channelled spectrum, and silver gives a fine fluted-looking spectrum in the blue. Chloride of calcium gives a striking set of six or seven bands between L and M, which may be seen both bright and reversed.

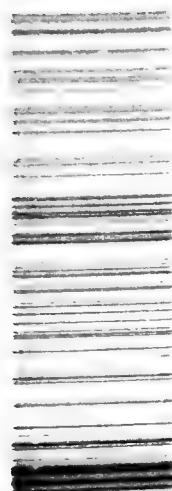
VI. Occasionally a double self-reversal of lines occurs, *i.e.* in the middle of the reversed or absorption line a bright line appears. We have many times seen this but not often photographed it. We have a plate which shews it in the case of the magnesium triplet between K and L. The photograph is that of the arc itself projected on to the slit of the spectroscope by a lens, and was taken at the moment when a piece of magnesium was dropped into the crucible. This has caused such an expansion of the bright lines that they have extended beyond the nearest two cyanogen bands and caused them to be reversed. On this bright background the magnesium lines themselves are reversed as a dark band in the centre of the field, and on this dark band are three narrow bright lines forming the second reversal. It is not difficult to understand how this occurs. The magnesium is very quickly evaporated and part of the vapour is driven by the expansion up the tube of the crucible before it has got very hot, and it drives before it some hotter vapour previously in the hottest part of the crucible. The cool vapour stops the radiation of the arc and the hotter vapour in front of it of course appears bright. The effect is little more than momentary. In this case the cool vapour was only just around the arc, for at top and bottom the same narrow lines which are bright in the middle of the field (black in the negative photograph) are reversed in the top and bottom.

It is worthy of remark that the facility of reversal of lines appears, speaking generally, to increase as the wave-length diminishes. This is very notable in the case of iron. It seems as if the fundamental vibrations, *i.e.* those most easily assumed by the molecule of the metal in a free state, were in the higher region of the spectrum. As if in fact they might be vibrations of which we have as yet perceived only lower harmonics. The great line of magnesium at wave-length 2852 certainly seems a fundamental one, if we may judge by its persistence, strength, and facility of reversal.

It is, however, by no means always the strongest lines which are most easily reversed, but rather those which are both persistent and strong. The ultra-violet lines of iron, which are so expanded and reversed in our photographs, are present, but not at all specially conspicuous, amongst the lines in the spectrum of the spark, but they are strong lines always in the arc. It seems as if in the spark, especially when a Leyden jar is used, violence were done to the metals, different in some way from that due to mere elevation of temperature, which gave them violent vibrations but not exactly those which they most readily take up when under less constraint. It is remarkable how easily the well-known pair of aluminium lines between H and K are reversed in the arc as well as the other pairs near S and above, and yet the metal in the arc does not shew at all either the triplet near N (*w. l.* about 3585, 3598, 3605) or the lower lines which are strong in the spark spectrum.



Mg 2852



U 2947



T 3020

S 3100

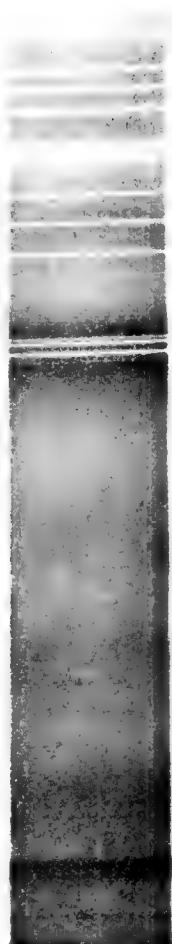


PLATE I. The left-hand photograph shews at top self-reversal of *Mg* line w.l. 2852.
The right-hand shews the same line enormously expanded and the iron lines between *U* and *S* reversed against the bright wing of the expanded line.

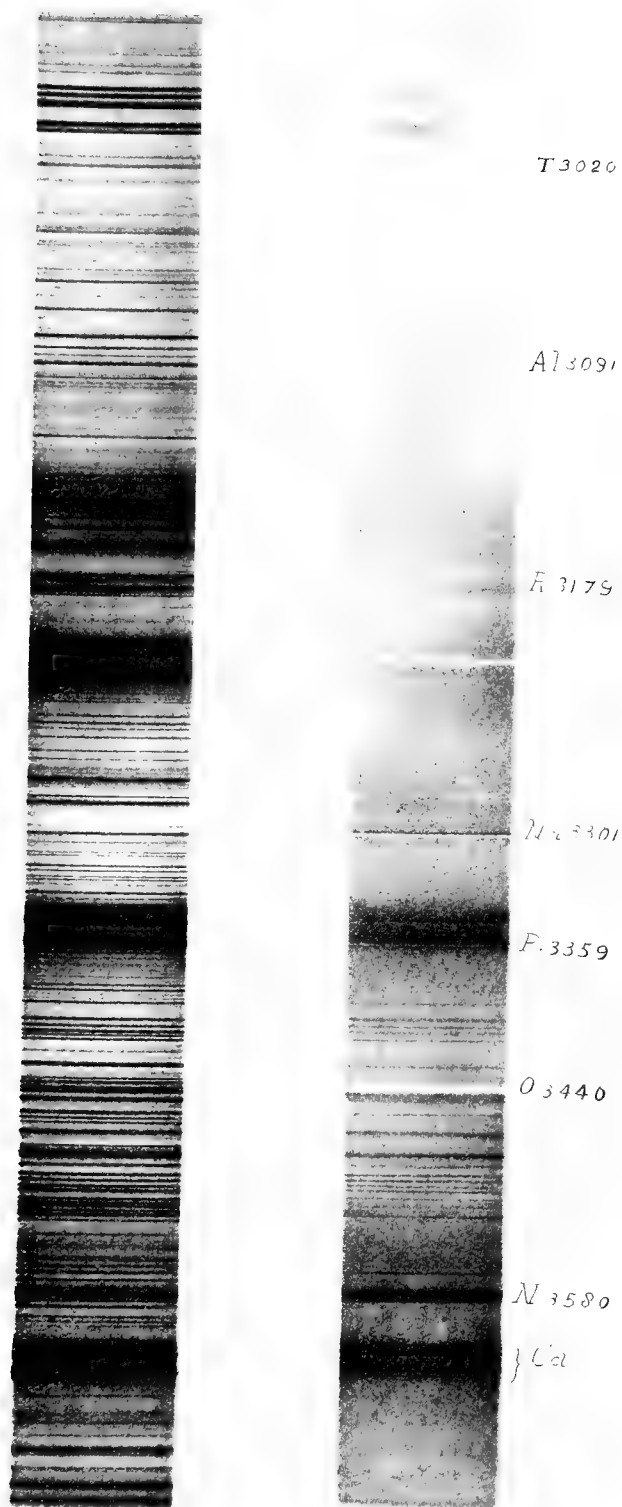


PLATE II. The right-hand photograph shews the potassium lines reversed, one sodium line being also reversed, and, less strongly, two calcium triplets.

The left-hand photograph shews the spectrum of the arc before the potassium salt was introduced.

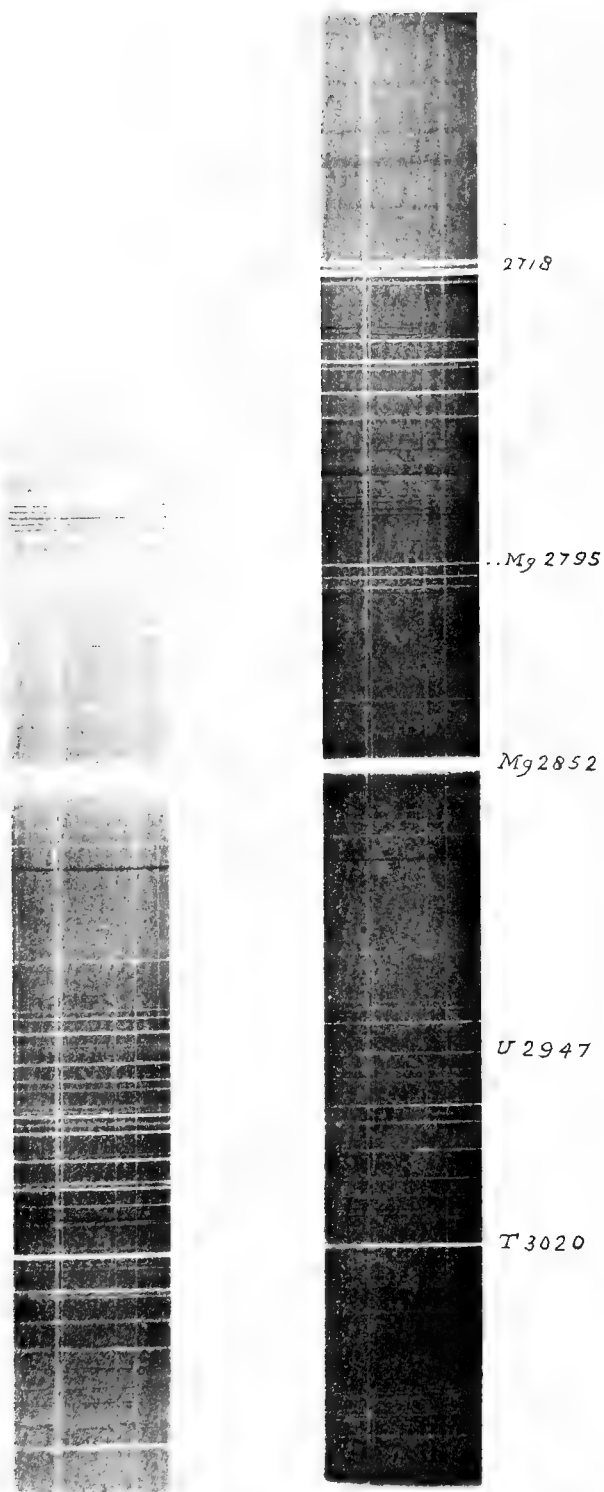


PLATE III. Shews iron lines reversed by introducing potassium ferrocyanide into the arc.

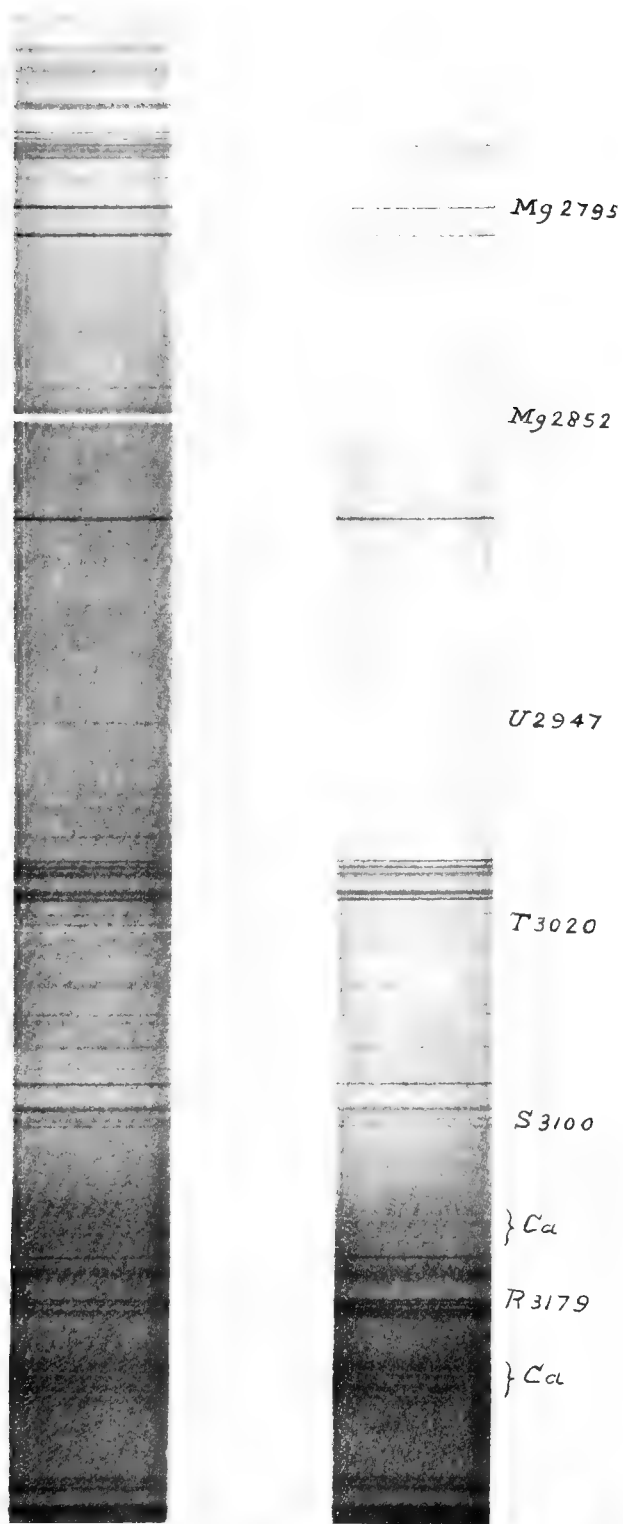


PLATE IV. Shews reversal of iron and other lines by a gentle stream of coal gas.

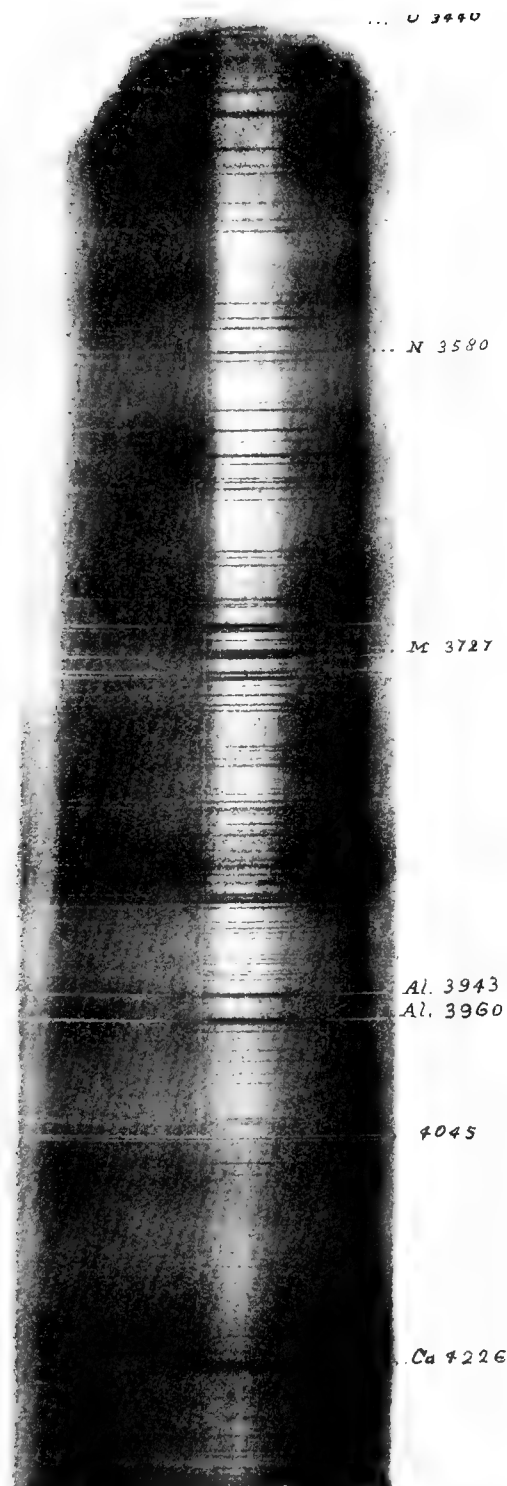


PLATE V. Shews iron and other lines reversed against the hot walls of a carbon tube. In the middle, where there was no background, the same lines are seen unreversed.

The quantity of metallic vapour is of course much less in the spark than in the arc, but it is much more violently, probably much more irregularly, agitated.

A very important factor in chemical action is the pressure to which the materials are subject, and we have not overlooked its importance in regard to solar chemistry. The difficulties of operating at pressures differing much from that of the atmosphere have hitherto delayed the extension of our observations in that direction, but we hope that those difficulties will not prove insuperable and that we shall be able on a future occasion to lay before the Society some observations on the effects of pressure on the phenomena of reversals.

ON THE ORIGIN OF THE HYDROCARBON FLAME SPECTRUM

[*Proceedings of the Royal Society*, Vol. xxxiv. (1882), pp. 418 sqq.]

IN previous communications* to the Society we have described the spectra of what we believe to be three compound substances, viz., cyanogen, magnesium-hydrogen, and water.

In these investigations our chief aim has been to ascertain facts, and to avoid as far as possible adopting any special theory regarding the genesis of the spectra in question. Thus, in speaking of the magnesium-hydrogen spectrum, which consists of three sets of flutings closely resembling in character the flame spectrum of hydrocarbons, we remark :—" We have been careful to ascribe this line and its attendant series to a mixture of magnesium and hydrogen rather than to a chemical compound, because this expresses the facts, and we have not yet obtained any independent evidence of the existence of any chemical compound of those elements."

In dealing with the cyanogen spectrum, we sometimes refer to it as the "nitro-carbon spectrum," in order to convey that "we are dealing with a spectrum invariably associated with the presence of nitrogen and carbon, in such conditions that chemical union takes place." Finally, in summing up our observations on the spectrum of water, we remark :—" In writing of this and other spectra which we have traced to be due to compounds, we abstain from speculating upon the particular molecular condition or stage of combination or decomposition which may give rise to such spectra."

The difficulties we have met with in endeavouring exhaustively to clear up many apparently simple spectroscopic problems, on a basis of fact as opposed to theory, is further illustrated in the concluding remarks of our paper entitled "Investigations on the Spectrum of Magnesium," wherein the following passage occurs :—"The chemical atoms of magnesium are either

* "On the Spectra of the Compounds of Carbon with Hydrogen and Nitrogen." I and II. *supra*, pp. 85, 100. "On the Spectrum of Carbon," *sup.* p. 178. "General Observations on the Spectrum of Carbon and its Compounds," *sup.* p. 235. "On the Spectrum of Water," *sup.* pp. 115, 176. "Investigations on the Spectrum of Magnesium," *sup.* pp. 80, 125.

themselves capable of taking up a great variety of vibrations, or are capable by mutual action on each other, or on particles of matter of other kind, of giving rise to a great variety of vibrations of the luminiferous ether; and to trace satisfactorily the precise connexion between the occurrence of the various vibrations and the circumstances under which they occur, will require yet an extended series of observations." (*Supra*, p. 132.)

Specific spectra have been satisfactorily proved to emanate from the compound molecules of cyanogen, water, and magnesium-hydrogen, so far as we can interpret in the simplest way the many observations previously detailed. The fact that a fluted spectrum is produced under certain conditions, by a substance which does not give such a spectrum under other conditions, is of itself a proof that the body has either passed into an isomeric state or has formed some new compound; but we are not entitled to assert, without investigation, which of these two reasonable explanations of the phenomena is the true one. There is, however, a spectrum to which we have had occasion to refer in the papers on the spectra of the compounds of carbon, which closely resembles that of a compound substance, and which we, in common with some other spectroscopists, have been led to attribute to the hydrocarbon acetylene, without, however, being able to bring forward such rigid experimental proofs of its origin as we have adduced in the case of the three substances above referred to. In other words, the experimental evidence that the hydrocarbon flame spectrum is really due to a hydrocarbon was always indirect. Thus, we shewed that many flames containing carbon, such as those of hydrogen mixed with bisulphide of carbon or carbonic oxide, and the flame of cyanogen in air, did not give this spectrum, and these particular flames are known, from the investigations of Berthelot, to be incapable of generating acetylene under conditions producing incomplete combustion. On the other hand, we found that a flame of hydrogen mixed with chloroform, which easily generates acetylene, gives the hydrocarbon flame spectrum in a very marked manner, and it is known that the ordinary blow-pipe flame, in which the same spectrum is well developed, contains this hydrocarbon.

These and other experiments point to the intimate relation of hydrogen and carbon in the combined form of acetylene to the production of this spectrum during combustion. In our various observations on the spectrum of the electric arc taken in different gases, the flame spectrum was always noticed, and seemed to be independent of the surrounding atmosphere. In the mode in which those experiments were conducted, it was easily shewn that the carbons were never free from hydrogen, and that the gases always contained traces of aqueous vapour. Under these conditions acetylene is formed synthetically during the electric discharge, the line spectrum of hydrogen being absent; so that we were never convinced that the spectrum was not due to the former substance.

It is well to remark in passing, that our previous work on the spectrum of the carbon compounds was mainly directed to that particular spectrum which is characteristic of the flame of cyanogen, and only indirectly to the flame spectrum of hydrocarbon. We were further supported in connecting the latter spectrum with acetylene, by observing that cyanogen compounds are continuously formed when the arc discharge takes place in gases containing nitrogen, and that in all probability their formation is due, as Berthelot has shewn, to a reaction taking place between acetylene and nitrogen. Berthelot is positive in his assertions that cyanogen is never formed by a direct combination between carbon and nitrogen, and that any such apparent combination is due to impure carbon, or to the presence of an imperfectly dried gas; in other words, hydrogen is essential to the production of cyanogen under such conditions according to the views of Berthelot. Such considerations led us to suggest the following view, expressed at the time the experiments were made, as to the origin of the hydrocarbon flame spectrum.

"The mere presence of the latter spectrum feebly developed in the electric discharge in compounds of carbon supposed to contain no hydrogen, appears to us to weigh very little against the series of observations which connect this spectrum directly with hydrocarbons." (*Supra*, p. 93, l. 3.)

"The arc in the middle of a magnesia crucible often shews no trace of the hydrocarbon set, although the cyanogen bands are strong. If, however, puffs of air or carbonic acid are passed into the arc, the hydrocarbon lines are produced."

"When the hydrocarbon spectrum is strong the brilliancy and number of the cyanogen groups that are visible are undoubtedly increased, so that the one variety of vibrations seems to affect the other. This is easily accounted for by the chemical interaction which takes place between acetylene, nitrogen, and hydrocyanic acid. The hydrocarbon spectrum is brought out at once in the magnesia crucibles by moistening one of the poles. All such actions seem to shew that hydrogen is essentially connected with the production of this fluted spectrum just as nitrogen is with the cyanogen series." (*Supra*, p. 238.)

The fact that carbonic oxide, which is one of the most stable binary compounds of carbon, forms a distinct spectrum of a character similar to that of the flame spectrum, tended to support the view that the flame spectrum might originate with acetylene. The similarity in the character of the magnesium-hydrogen spectrum to that of the hydrocarbon flame spectrum induced us to believe that they were due to similarly constituted compounds, and inasmuch as we felt sure about the accuracy of the view which assigns the former spectrum to some compound of magnesium with hydrogen, we accepted the analogy in favour of the supposition that acetylene is the substance which produces the flame spectrum; or, at any rate, that acetylene is a necessary

concomitant of the reaction taking place during its emission, and consequently might give rise to this peculiar spectrum.

Having examined this question in the way described, we adopted the view* of Ångström and Thalén as to the genesis of this spectrum in opposition to the views of Attfield, Morren, Watts, Lockyer, and others, who held that this spectrum was really due to the vapour of carbon. The delicate character of the experiments which were required to discover the origin of the peculiar set of flutings in the more refrangible part of the spectrum of cyanogen made it apparent that, whatever views as to the origin of the hydrocarbon flame spectrum were adopted by different workers, experimental proof was still wanting to shew which was the correct one. In referring to the theory that carbon vapour is the cause of the peculiar spectrum of cyanogen, we remarked: "Now, the evidence that carbon uncombined can take the state of vapour at the temperature of the electric arc is at present very imperfect. Carbon shews at such temperatures only incipient fusion, if so much as that; and that carbon uncombined should be vaporised at the far lower temperature of the flame of cyanogen is so incredible an hypothesis that it ought not to be accepted if the phenomena admit of any other probable explanation." (*Supra*, p. 111, last par.)

With the object of being able to exhaust this question, a special study was subsequently made of the ultra-violet line spectrum of carbon, in order to ascertain whether any of its lines could be found in the spectra of the arc or flame. We have found that the ultra-violet lines of metallic substances have as a rule the greatest emissive power, and are often present when no trace of characteristic lines in the visible part of the spectrum can be detected. If carbon resembled the metals in this respect, then we might hope to find ultra-violet lines belonging to its vapour, thus enabling us to detect the volatilization of the substance at the relatively low temperatures of the arc and flame. The test experiments made on this hypothesis are recorded in the paper entitled "General Observations on the Spectra of Carbon and its Compounds" (*supra*, p. 235). It is there shewn that some seven of the marked ultra-violet spark lines of carbon† occur in the spectrum of the arc discharge, although one of the strongest lines, situated in the visible portion

* This view was first suggested by Plücker and Hittorf in the same paper in which they published the theory of spectra of different orders. They write:—"It appears doubtful that the different types depend solely upon temperature. If so, the temperature varying in the different parts of the ignited vapour of carbon, different types may be seen simultaneously. We shall not now discuss the influence which the coexistence of foreign gases might have on the spectra of the vapour of carbon, nor may we here decide whether or not in the lower temperature of the flame, a gaseous compound of carbon, not being entirely decomposed, exhibits with the spectra of the vapour of carbon simultaneously the spectrum of the undecomposed gas."—*Phil. Trans.*, 1865. (Jan. 26, 1883.)

† Subsequently it appeared that only one of these lines is due to carbon, the other six belong to silicon (*supra*, p. 230).

of the spectrum at wave-length 4266, could not be found. Further, it is proved that the strongest ultra-violet line of carbon does occur in the spectrum of the flame of cyanogen fed with oxygen. Thus it seems probable that the same kind of carbon molecule exists, at least in part, in the arc and flame, as is found to be produced by the most powerful electric sparks, taken between carbon poles or in carbon compounds.

Now the spark gives us the spectrum which is associated with the highest temperatures, and therefore it is assumed that this spectrum is that of the simplest kind of carbon vapour. If that be the case, we cannot avoid inferring that denser forms of carbon vapour may exist in arc and flame, emitting, like other complex bodies, a fluted, in contrast to a line, spectrum; or rather that the two distinct kinds of spectra may be superposed. Such considerations shewed that a series of new experiments and observations must be made with the special object of reaching a definite conclusion regarding the origin of the flame spectrum, and the following pages contain a summary of the results of such an inquiry.

Vacuous Tubes.

We have heretofore laid little stress on observations of the spark in vacuous tubes on account of the great uncertainty as to the residual gases which may be left in them. The film of air and moisture adherent to the glass, the gases occluded in the electrodes, and minute quantities of hydrocarbons of high boiling-point introduced in sealing the glass, may easily form a sensible percentage of the residue in the exhausted tube, however pure the gas with which it was originally filled. The excessive difficulty of removing the last traces of moisture we learnt when making observations on the water spectrum, and the almost invariable presence of hydrogen in vacuous tubes is doubtless due in great measure to this cause. Wesendonck (*Proc. Roy. Soc.*, vol. xxxii, p. 380) has fully confirmed our observations as to this difficulty. By a method similar to that employed by him, we have, however, succeeded in so far drying tubes and the gases introduced into them that the hydrogen lines are not visible in the electric discharge. For this purpose the (Plücker) tube was sealed on one side to a tube filled for some six or eight inches of its length with phosphoric anhydride through which the gas to be observed was passed, and on the other side to a similar tube full of phosphoric anhydride, which was in turn connected by fusion to the (Sprengel) pump. To dry the gas it is not enough to pass it through such a tube, or even a much longer one; full of phosphoric anhydride; it has to be left in contact with the anhydride for several hours, and to get the adhering film of moisture out of the tube it has to be heated after exhaustion, while connected as above described with the drying tubes, up to the point at which the glass begins to soften, and kept at near this temperature for some time. To get most of the gases out of the electrodes the tube must be exhausted and sparks passed

through it for some time before it is finally filled with the gas to be observed. Even when these precautions have been taken, the lines of hydrogen can often be detected in tubes filled with gases which should contain no hydrogen. The general result of our observations on the spectra observed in tubes so prepared is that the channelled spectrum of the flame of hydrocarbons is not necessarily connected with the presence of hydrogen* ; it does not come and go according as hydrogen is or is not present along with carbon in the way that the channelled spectrum of cyanogen comes and goes according as nitrogen is present or absent. Our observations confirm those of Wesendonck on this point.

A tube filled with hydrogen containing a small percentage of cyanogen and exhausted, was found to give plainly the seven channellings in the blue and six channellings in the indigo characteristic of cyanogen, and the hydrogen lines of course strongly, but no more than a trace of the brightest green line of the spectrum of the flame of hydrocarbons. The use of a Leyden jar brought out no more. Continued sparking made no sensible difference, the cyanogen spectrum remained, the green line did not alter : and no other line of the spectrum of the hydrocarbon flame appeared.

Tubes filled with carbonic oxide exhibit in general at different stages of exhaustion the following phenomena. When the exhaustion is commencing and the spark will just pass, the spectrum of the discharge in the capillary tube is usually that of the flame of hydrocarbons and nothing else. As the exhaustion proceeds the spectrum of carbonic oxide makes its appearance superposed on the former, and gradually increases in brilliance until it overpowers and at last, at a somewhat high degree of exhaustion, entirely supersedes the flame spectrum. This is when no jar is used. In the earlier stages of exhaustion the effect of the jar is to increase the relative brilliance of the flame spectrum and diminish that of the carbonic oxide spectrum, and at the same time to bring out strongly the lines of oxygen and carbon ; at a certain stage of the exhaustion, when the flame spectrum is very weak without the jar, the effect of the jar is to bring it out again but without sensibly enfeebling the carbonic oxide spectrum, and without bringing out the carbon lines. At a still higher stage of exhaustion, when the carbonic oxide spectrum alone is seen without the jar, the flame spectrum is sometimes, not always, brought out by putting on the jar, though the carbon lines again shew well. At this stage, at which the flame spectrum is not seen at all, the distance between the striæ in the wide part of the tube is considerable, and much metal is thrown off the electrodes, which are rapidly heated by the

* This statement may have to be qualified if the spectrum described as the second spectrum of hydrogen by Plücker and Hittorf and by Wüllner, and recently further investigated by Hasselberg (*Mém. Imp. Acad. Sc.*, St Petersburg, xxx, No. 7), be the most persistent spectrum of hydrogen at low pressures ; because the statement in the text is based on the supposition that hydrogen could be detected with certainty by the "C" or "F" line. (Jan. 26, 1883.)

discharge. Some of these tubes were filled with carbonic oxide made by heating a mixture of potassium oxalate and lime contained in a prolongation of the tube containing the phosphoric anhydride. Others were filled from a mixture of sodium oxalate and sulphuric acid heated in a flask sealed to a long tube which had the middle part filled with quicklime and the two ends filled with phosphoric anhydride; and after all the air was expelled and the flask had been sealed off, the quicklime was heated to absorb the carbonic acid. These tubes shewed no trace of the cyanogen flutings at any stage of exhaustion, either to the eye or in photographs of the spectrum. Nevertheless, in the earlier stages of exhaustion, some of such tubes do shew, when the jar is used, a group of three lines in the indigo which is seen in the flame of cyanogen, and has formerly been described by us as part of the spectrum of cyanogen. We must now, however, retract the opinion that this group is due to cyanogen. We have before noted (*supra*, pp. 236, 238) that these three lines are seen under many different circumstances when the cyanogen flutings are absent, and as the flutings also are frequently seen without the three lines, it seems that the three lines belong to some other spectrum than the flutings, and as we have now found them where nitrogen has been carefully excluded, we are forced to attribute them either to carbon or some compound other than cyanogen.

In one case a very little copper-nitride was introduced into one end of the drying tube, and after the whole had been filled with gas and the generating flask sealed off, the nitride was heated so as to mix a small quantity of nitrogen with the carbonic oxide. In the spectrum of this tube the cyanogen flutings were not visible to the eye, but the ultra-violet set between K and L came out plainly in the photographs. No hydrogen line could be detected in it. This is remarkable, because Berthelot did not find that cyanogen is generated by electric sparks in a mixture of nitrogen and carbonic oxide unless hydrogen be also present. It would, however, be rash to assume that no trace of hydrogen was present because the lines of hydrogen were not visible in the spectrum, since we know by experience that the electric discharge does not always light up all that is in a tube. Mercury, for instance, must be present in all these tubes, but its lines do not usually shew until the exhaustion is carried to a high degree.

One tube was filled with nitrogen with which was mixed a small percentage of cyanogen obtained by heating a little mercury-cyanide placed at one end of the drying tube. This tube gave well the channellings in the blue and indigo characteristic of cyanogen, but neither the hydrogen lines nor the spectrum of the hydrocarbon flame. The cyanogen seems to be scarcely at all decomposed by the spark when thus diluted, for the carbon lines were not brought out by the use of a jar, and the cyanogen spectrum remained after continued sparking. We remark that Berthelot found it

exceedingly difficult to get acetylene from a mixture of cyanogen and hydrogen at atmospheric pressure; and in order to make this experiment succeed, short and very powerful sparks had to be continued for some hours.

In a tube filled with carbonic oxide mixed with a little air imperfectly dried, when not too highly exhausted, the carbonic oxide spectrum, that of the flame of hydrocarbons, and that of cyanogen, may all be seen at once superposed when no jar is used. With a jar and a tolerably high exhaustion the carbonic oxide spectrum, the hydrocarbon flame spectrum, and the carbon line spectrum, may all be seen at the same time. All the foregoing observations were made when the tubes were viewed end on and the image of the narrow part of the tube thrown on the slit by a lens. Tubes filled with carbon disulphide and carbon tetrachloride at reduced pressures have been examined by us, but these compounds of carbon are very quickly decomposed by the spark, so that few observations can be made with one tube. If the exhaustion is not carried very far the spectrum of the hydrocarbon flame is seen both in carbon disulphide and in carbon tetrachloride, when all the precautions above-mentioned have been taken to remove moisture, and when no trace of the hydrogen spectrum is visible. At higher exhaustions the spectrum is a faint continuous one together with that of sulphur or chlorine as the one or other is present. The spark taken without condenser between electrodes near together in wide tubes filled with saturated vapour of carbon disulphide or carbon tetrachloride dried with phosphoric anhydride, and deprived as completely as possible of air by pumping or boiling out, shews the spectrum of the flame of hydrocarbons brightly; but in tubes filled with carbonic acid gas from ignited sodium carbonate and boric anhydride and sealed off at a high temperature, the spectrum is that of carbonic oxide together with that of oxygen.

Spectrum of the Spark in Compounds of Carbon at Higher Pressures.

In the spark taken between poles of purified graphite in hydrogen, the spectrum of hydrocarbon flames is seen, and it increases in brilliance as the pressure of the gas is increased up to ten atmospheres, and continues bright at still higher pressures so far as we have observed, that is, up to twenty atmospheres. The spark without condenser in carbonic oxide at atmospheric pressure, shews both the spectrum of carbonic oxide and that of the hydrocarbon flame; and as the pressure of the gas is increased, the former spectrum grows fainter, while the latter grows brighter, no jar being used. The line spectrum of carbon is also visible. At the higher pressures the flame spectrum predominates and is very strong. The observations were carried up to a pressure of twenty-two and a half atmospheres. On letting down the pressure, the same phenomena occur in the reverse order. All the parts of the flame spectrum, as seen in a Bunsen burner, are increased

in intensity as the pressure is increased. The fact that the effects of high pressure are so similar to those produced by the use of a condenser at lower pressures, seems to point to high temperature as the cause of those effects. But against this, we have the fact that at reduced pressure we get, in carbonic oxide, the carbonic oxide spectrum and the line spectra of carbon and oxygen simultaneously, without that of the hydrocarbon flame. As we cannot doubt that a very high temperature is required to give the line spectrum of carbon, we must suppose that reduced pressure is unfavourable to the stability of the molecular combination, whatever it be, which gives the hydrocarbon flame spectrum. Wesendonck has remarked (*loc. cit.*) that in carbonic acid at pressures too low for the flame spectrum to be developed without a jar, it is only in the narrow part of the tube that the use of a jar brings out that spectrum. It would appear, therefore, that the constraint, due to the confined space in which the discharge occurs, has the same effect, in regard to the stability of the combination producing the spectrum in question, as increase of pressure.

Cyanogen Flame Spectrum.

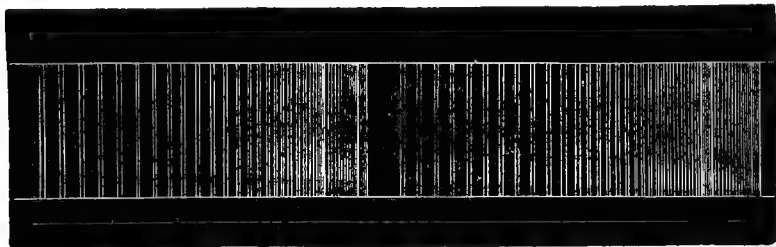
Our former observations "On the Flame Spectrum of Cyanogen burning in Air" (*supra*, p. 90) were made on cyanogen gas, prepared from well-dried mercury cyanide, which was passed over phosphoric anhydride, and burnt from a platinum jet fused into the end of the tube. We observed what Plücker and Hittorf had noted, that the hydrocarbon bands were almost entirely absent, only the brightest green band was seen, and that faintly. When gaseous cyanogen is liquefied by the direct pressure of the gas, the researches of Gore (*Proc. Roy. Soc.*, vol. xx, p. 68) have shewn that it is apt to be contaminated with a brownish, treacly liquid, which probably arises from the imperfectly purified or dried cyanide of mercury. In order to obtain pure cyanogen we have prepared quantities of liquid cyanogen, not by compression, but by passing the already cooled gas into tubes placed in a carbonic acid and ether bath. By this method of condensation any easily liquefiable substances are isolated, and any permanently gaseous substance escapes. The samples were sealed up in glass tubes into which different reagents were inserted. After such treatment the cyanogen was used for the production of the flame in dry air or oxygen. The liquid cyanogen was left in contact with phosphoric anhydride, Nordhausen sulphuric acid, and ordinary sulphuric acid. By means of a special arrangement of glass tubing surrounding the flame dry oxygen could be supplied, or oxygen made directly from fused chlorate of potash could, by means of a separate nozzle, be directed on to the flame, and thus perfectly dry and pure gases used for combustion. Liquid cyanogen which had remained in presence of the above reagents gave only the single green hydrocarbon line faintly in dry air, all the cyanogen violet sets being strong. When oxygen made directly from the chlorate of potash was directed

on to the flame, all the hydrocarbon flame sets appeared with marked brilliancy. The set of lines which we have formerly referred to as the three lines or set of three flutings of the cyanogen spectrum, shew marked alteration of brilliancy with variations in the oxygen supply. Thus liquid cyanogen, purified by the action of the above reagents, does yield the spectrum of hydrocarbons on combustion in pure oxygen. From the great precautions we have taken we feel sure that the amount of combined hydrogen in the form of water or other impurities in the combining substances must have been exceedingly small, and that the marked increase in the intensity of the flame spectrum when oxygen replaces air is essentially connected with the higher temperature of the flame, and is not directly related to the amount of hydrogen present. This being the case, it must be admitted that the hydrocarbon flame spectrum requires a higher temperature for its production during the combustion of cyanogen than that which is sufficient to cause a powerful emission of the special spectrum of the molecules of cyanogen. Now the two compounds of carbon which give the highest temperature on combustion are cyanogen and acetylene. Both of these compounds decompose with evolution of heat, in fact they are explosive compounds, and the latent energy in the respective bodies is so great that if kinetic in the separated constituents it would raise the temperature between three and four thousand degrees. The flames of cyanogen and acetylene are peculiar in respect that the temperature of individual decomposing molecules is not dependent entirely on the temperature generated by the combustion which is a function of the tension of dissociation of the oxidised products, carbonic acid and water. We have no means of defining with any accuracy the temperature which the particles of such a flame may reach. We know, however, that the mean temperature of the flames of carbonic oxide and hydrogen lies between two and three thousand degrees, and if to this be added that which can be reached independently by the mere decomposition of cyanogen or acetylene, then we may safely infer that the temperature of individual molecules of carbon, nitrogen, and hydrogen in the respective flames of cyanogen and acetylene may reach a temperature of from six to seven thousand degrees.

A previous estimate of the temperature of the positive pole in the electric arc made by one of us, gave something like the same value.

Further evidence of the high temperature of the cyanogen flame is afforded by the occurrence in the spectrum of that flame, when fed with oxygen, of a series of flutings in the ultra-violet, which appear to be due to nitrogen. The series consists of four, or perhaps more, sets, each set consisting of a double series of lines overlapping one another. The lines increase in their distance apart on the more refrangible side, otherwise the flutings have a general resemblance to the B group of the solar spectrum. The figure overleaf gives the general appearance of two of the sets, but is not drawn to a scale.

The four sets commence approximately at about the wave-lengths 2718, 2588, 2479, 2373 respectively. They are frequently present in the spectrum of the arc taken in a magnesia crucible, and shew strongly in that of the spark taken without a condenser either in air or nitrogen. As they appear in the spectrum of the spark in nitrogen, whether the electrodes be aluminium or magnesium, and do not appear when the spark is taken in hydrogen or in carbonic acid gas, they are in all probability due to nitrogen. When a large condenser is used they disappear.



The formation of acetylene in ordinary combustion seems to be the agent through which a very high local temperature is produced, and this is confirmed by the observations of Gouy on the occurrence of lines of the metals in the green cone of the Bunsen burner, which are generally only visible in spark spectra; on this view acetylene is a necessary agent in the production of the flame spectrum during combustion. The fact that when the arc is taken in a magnesia crucible, although the cyanogen spectrum is strong, the flame spectrum is often invisible, but may be made to appear by introducing a cool gas or moisture, may be accounted for by an increased resistance in the arc producing temporarily a higher mean temperature. Experiments in course of execution, where the arc will be subject to a sudden increase of pressure, will, we trust, solve this problem.

Electric Discharge between Graphite Poles in different Gases.

When pure graphite is employed, instead of the ordinary carbon poles, and the arc discharge is taken in different gases, in the same way as was described in our first paper, "On the Spectra of the Compounds of Carbon" (*supra*, pp. 87 sqq.), we have noticed some slight differences which are worthy of record. In carbonic acid gas, fine channellings are seen covering the whole extent of the spectrum from the low red as far as the blue set of the flame spectrum, the flutings of the one group being observable as far as the next group. The triple set of the cyanogen flame spectrum remained very strong when all the cyanogen groups in the violet had disappeared. When the carbonic acid is displaced by hydrogen, the hydrogen lines appear, the hydrocarbon flame and the triple

sets remaining bright ; but in this gas the flame group at 431 is particularly well marked, and the carbon line at 4266 keeps flashing in occasionally. Thus we have in the same field of view the hydrocarbon series, the hydrogen lines, and one of the strongest lines of carbon. The De Meritens intermittent arc discharge was employed in these experiments, and it is curious to note that hydrogen, instead of favouring the passage of the arc between carbon poles, really introduces some peculiar resistance, perhaps owing to the reduction of temperature by the gas surrounding the arc, or because of the formation of acetylene. The arc is at any rate much shorter and smaller in section than in air, but the temperature seems to be correspondingly increased, as we may infer from the fact that the hydrogen and carbon lines are now very marked. The Siemens arc in air does not shew the carbon line at 4266, although we have proved that some of the chief ultra-violet lines occur in this discharge. The arc taken in carbonic oxide shews the triple group along with the usual sets of the hydrocarbon flame spectrum, without any trace of the carbonic oxide spectrum being visible. The occurrence of the triple set of lines, in the absence of other groups characteristic of cyanogen, makes us doubt whether this set has anything really to do with nitrogen. We are inclined to think that their previous appearance when the arc was taken in glycerine containing nitro-benzene was really due to some indirect effect, and ought not to be taken as proof of the formation of cyanogen in the absence of other characteristic groups under such circumstances.

NOTE ON THE ORDER OF REVERSIBILITY OF THE
LITHIUM LINES

[*Proceedings of the Royal Society*, Vol. xxxv. (1883), p. 76]

IN our communications on the reversal of the lines of metallic vapours we have several times noticed (*supra*, pp. 24, 28, 36) the reversal of the lithium lines, and concluded that the blue line is more easily reversed than the orange line. This, however, does not appear to be really the case. When much lithium is introduced into the arc, a second blue line is developed close to but slightly more refrangible than the well-known blue line. This second blue line produces with the other the appearance of a reversal, which deceived us until we became aware of the existence of the second line. The blue line (wave-length 4604) is really reversed without difficulty when sufficient lithium is present, but under these circumstances the orange line is also reversed. The latter line is also the one which first (of the two) shews reversal, and also the one which is more persistently reversed. Hence we place the lines in order of reversibility as follows: red, orange, blue, green, violet.

NOTE ON THE REVERSAL OF HYDROGEN LINES; AND ON
THE OUTBURST OF HYDROGEN LINES WHEN WATER
IS DROPPED INTO THE ARC

[*Proceedings of the Royal Society*, Vol. xxxv. (1883), pp. 74 sqq.]

THE concentration of the radiation of hydrogen in a small number of spectral lines would lead us to expect that the absorption of light of the same refrangibility as those lines would, at the temperature of incandescence, be correspondingly strong, and that therefore the hydrogen lines would be easily reversed. The mass of hydrogen which we can raise to a temperature high enough to shew the lines is, however, so small, that notwithstanding the great absorptive power of hydrogen for the rays which it emits, the reversal of the lines has not hitherto been noticed. We find, in fact, that the lines are very readily reversed, and the reversal may be easily observed.

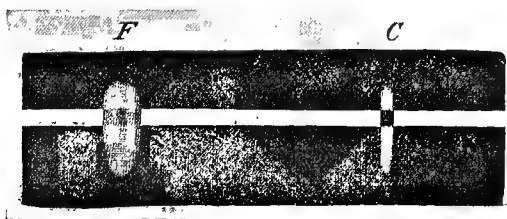
When a short induction spark is taken between electrodes of aluminium or magnesium in hydrogen at atmospheric pressure, a large Leyden jar being connected with the secondary wire of the coil, the hydrogen lines shew no reversal; but if the pressure of the hydrogen be increased by half an atmosphere or even less*, the lines expand and a fine dark line may be seen in the middle of the F line. As the pressure is increased this dark line becomes stronger, so that at two atmospheres it is very decided. As the F line expands with increase of pressure the dark line expands too and becomes a band. It is best seen when the pressure is between two and three atmospheres. When the pressure is further increased the dark band becomes diffuse, and at five atmospheres cannot be distinctly traced. No definite reversal of the C line was observed under these circumstances. The dispersion used, however, was only that of one prism.

By using a higher dispersion the reversal of both the C and F lines may be observed at lower pressures. For this purpose we have used a Plücker

* The pressures here mentioned are only measured by a metallic gauge attached to the Cailletet pump employed, and must therefore be taken as only approximately correct.

tube, filled with hydrogen and only exhausted until the spark would pass readily when a large jar was used.

The light of the narrow part of the tube is, under these circumstances, very brilliant, while the spark in the broad ends is wider and less bright, but does not fill the tube. On viewing such a tube end on, and projecting the image of the narrow part of the tube on to the slit of the spectroscope, a continuous spectrum, of the width of the image of the narrow part of the tube, is seen, besides the lines of hydrogen given by the discharge in the wide part of the tube. These lines extend above and below the narrow continuous spectrum if the electrode is well placed so that half-an-inch or so of the spark in the wide part of the tube may intervene between the narrow part of the tube and the spectroscope. The continuous spectrum of the narrow part of the tube seems due chiefly to the expansion of the hydrogen lines when the discharge occurs in so confined a space, and it is much brighter than the lines given by the spark in the wide part of the tube. Where the latter cross the continuous spectrum a very evident absorption occurs. We have observed it with a diffraction grating. The C line in the third order falls so near the



F line in the fourth, that both may be observed together. The appearance presented in our spectroscope is shewn in the accompanying drawing; F is much more expanded than C, and the reversal consequently less marked though quite plain. The other lines being still more diffuse their absorption could not be traced.

We have before observed (*supra*, p. 89) that the C and F lines of hydrogen are visible in the arc of a De Meritens magneto-electric machine taken in hydrogen; though in the arc of a Siemens machine the C line can only be detected at the instant of breaking the arc, the F line hardly at all. When, instead of taking the arc in hydrogen, small drops of water are allowed to fall from a fine pipette into the arc taken in air in a lime crucible, each drop as it falls into the arc produces an explosive outburst of the hydrogen lines. Generally the outburst is only momentary, but occasionally a sort of flickering arc is maintained for a second or two and the hydrogen line C is visible all the time. The lines (C and F) are usually much expanded, but are frequently very unequally wide in different parts of the line. F is

weaker, more diffuse, and more difficult to see than C, and is visible for a shorter time. There is no sign of reversal. In the explosive character of the outburst and the irregularity in the width of the lines, the effect resembles that of an outburst of hydrogen in the solar atmosphere. The elements of the water are, as we must suppose, separated in the arc, but from the explosive character of the effect they are not uniformly distributed in the arc. The arc being horizontal and the image of it projected on to the slit of the spectroscope, it was really a very small section of the arc which was under observation, and this renders the variation in the width of the lines the more remarkable.

NOTES ON THE ABSORPTION OF ULTRA-VIOLET RAYS BY VARIOUS SUBSTANCES

[*Proceedings of the Royal Society*, Vol. xxxv. (1883), pp. 71 sqq.]

THE following notes contain some records of ultra-violet absorptions in addition to those which have been examined by Soret, Hartley, M. de Chardonnet, and other investigators. For these observations we have generally used the spark of an induction-coil, with Leyden jar, between iron electrodes as the source of light. Occasionally we have used other electrodes, but the lines of iron are so multitudinous, and so closely set in a large part of the ultra-violet region of the spectrum, that they form almost a continuous spectrum, at the same time there are amongst them a sufficient number of breaks and conspicuous lines to serve as points of reference. The spectroscope has a single prism of quartz, and the telescopes have quartz lenses. The image of the spark was projected on to the slit of the spectroscope by a quartz lens, and the absorbent substances were interposed between the slit and the last-mentioned lens. The gases were held in tubes fitted, some with quartz, others with rock salt, plates on the ends; liquids in cells with quartz sides. The spectra were all photographed.

Chlorine in small quantity shews a single absorption band extending from about N (3580) to T (3020). As the quantity of chlorine is increased this band widens, expanding on both sides, but rather more rapidly on the less refrangible side. Different quantities of chlorine produced absorption from about H (3968) to wave-length 2755, from wave-length 4415 to 2665, and from wave-length 4650 to 2630. With the greatest quantity of chlorine tried the absorption did not extend above wave-length 2550.

Bromine vapour in small quantity absorbs light up to about L (3820), and is quite transparent above that. With larger quantity the absorption increases, gradually extending with increase of bromine vapour from L to P (3360); and at the same time there is a gradually increasing general absorption at the most refrangible end of the spectrum beginning at about wave-length 2500; so that the denser bromine vapour is transparent for a band between wave-length 2500 and 3350.

Liquid bromine in very thin film between two quartz plates is transparent for a band between wave-length about 3650 and 3400, shading away on both sides, so that below M on one side and above P on the other the absorption seems complete. The transparency of the liquid film ends on the more refrangible side just where that of the vapour begins.

Iodine vapour tolerably dense cuts off all within the range of our photographs below wave-length 4300, and its absorption gradually diminishes from that point up to about wave-length 4080; from that point it is transparent*. Denser vapour produces complete absorption up to 4080 and partial absorption above that point.

Iodine dissolved in carbon disulphide is transparent for a band between G and H, cutting off all above and below. It is not possible to tell how much of the light above M (3727) is absorbed by iodine in such a solution, inasmuch as carbon disulphide is opaque for rays more refrangible than M.

Iodine dissolved in carbon tetrachloride, when the solution is weak, shews only the absorption due to the solvent, described below. More iodine increases the absorption until it is complete above P (3360), with shading edge as far down as about wave-length 3400.

Sulphurous acid gas produces an absorption band which is very marked between R (3179) and wave-length 2630, and a fainter absorption extending on the less refrangible side to O (3440), and on the other side to the end of the range photographed, wave-length 2300.

Sulphuretted hydrogen produces complete absorption above wave-length 2580. Below that a partial general absorption.

Vapour of carbon disulphide in very small quantity produces an absorption band extending from P to T, shading away at each end; no absorption in the higher region. With more vapour the absorption band widens, extending from about wave-length 3400 to 3000, and a second absorption occurs beginning at about wave-length 2580, and extending to the end of the range photographed.

Carbon tetrachloride liquid produces an absorption band with a maximum about R, extending, but with decreasing intensity, up to Q (3285) on one side, and to s (3045) on the other. In the higher region there is a second absorption sensible about wave-length 2600, and increasing in intensity up to about wave-length 2580, beyond which point it is complete.

Chlorine peroxide gives a succession of nine shaded bands, at nearly equal

* The principal absorption band of the haloids seems to shift towards the less refrangible side with increase of atomic weight, and so to agree with the general rule which Lecoq de Boisbaudran has noticed in the shifting of corresponding lines in the spectra of groups of similar metals.—March 16.

intervals, between M and S, with faint indications of others beyond. In the highest region this gas seems quite transparent.

A slice of chrome-alum a quarter of an inch thick is transparent between wave-length 3270 and 2830, its absorption gradually increases on both sides of those limits, but rather more rapidly on the more refrangible side than on the other, and becomes complete below about wave-length 3360 and above wave-length 2730.

A very thin plate of mica shews absorption beginning about S (3100), rapidly increasing above U (2947), and complete above wave-length 2840.

A thin film of silver precipitated chemically on a plate of quartz transmits well a band of light between wave-length about 3350 and 3070, but is quite opaque beyond those limits on both sides*.

A thin film of gold similarly precipitated merely produces a slight general absorption all along the spectrum.

The difference between the limits of transparency of Iceland spar for the ordinary and extraordinary rays, inferred from theory by Lommel, we find to be very small, and hardly to be detected without using a considerable thickness, three inches or more, of the spar.

We had expected to be able to apply the well-known photometric method by means of polarised light to the comparison of intensities of ultra-violet rays. Ordinary Nicol's prisms are not applicable to ultra-violet rays on account of the opacity of the Canada balsam, with which they are cemented, but through the kindness of the President of the Society, we obtained from him the loan of a pair of Foucault's prisms. Upon taking photographs of the spectrum of the iron spark through this pair of prisms at various inclinations between the planes of polarisation of the two prisms, we found that for the whole range between the position of parallelism and the inclination of 80° there was no sensible difference of effect upon the photographic plate, though the length of exposure was in all cases the same. For inclinations between 80° and 90° there was a sensible and increasing diminution in the photographic effect as the planes of polarisation of the polariser and analyser were more nearly at right angles to one another. It seems to follow from this that the full photographic effect on the dry gelatine plates used by us ensues when the intensity of the light reaches a certain limit, but that for intensities of light beyond that limit there is no sensible increase in the effect until the stage of solarisation is reached.

* Cornu has noticed (*Spectre Normal du Soleil*, p. 23, note) that such a film of silver is transparent for certain ultra-violet rays, but he places them about wave-length 270, which does not agree with our observations. Chardonnet (*Comp. Rend.*, February, 1883) says that the transparent band extends from O to S. W. A. Miller (*Phil. Trans.*, 1863) noticed that for a certain distance in the ultra-violet a silver reflector did not reflect the incident rays.

THE ULTRA-VIOLET SPECTRA OF THE ELEMENTS

[*Proceedings of the Royal Institution*, Vol. x. (1883), pp. 245 sqq.]

It seems probable that the range of our vision as regards colour is closely connected with the intensity of that part of the solar radiation which reaches us on the earth, for Langley's observations on the intensity of the sun's rays in different parts of the spectrum bring out the fact that the region of greatest intensity falls nearly in the middle of the visible spectrum, and includes those colours to which our eyes are most sensitive. The ultra-violet rays, those which lie beyond the violet on the more-refrangible side, are not, however, absolutely invisible, for, by carefully excluding light of lower refrangibility, Herschel found that he could see some distance beyond the Fraunhofer line H, into what he called the lavender-grey; and Helmholtz has succeeded in seeing nearly all the strong lines in the solar spectrum almost or quite up to its limit. Still these rays may fairly be said to be beyond ordinary vision; and from their power of chemical action they used to be distinguished as "actinic" rays. We know now that they have no monopoly of chemical activity, and we recognise no difference between luminous and actinic rays, the visible and the ultra-violet, except in their oscillation frequencies; that is, in the rate at which the successive pulsations of the ray succeed one another, and in the colour and refrangibility which are directly dependent on that rate. That the ultra-violet part of the solar spectrum extended at least as far above the line H as F is below it, has been known since the time of Wollaston, who observed its effect in blackening silver salts; but it is only about twenty years since Stokes made known to us the great length and intensity of the ultra-violet spectrum of the electric spark. Stokes used his own invention, a fluorescent screen, for observing the rays; and at the very time when Stokes published his discovery, W. A. Miller published photographs of the spectra of sparks taken between various metallic electrodes. Both these methods, that of fluorescent screens and that of photography, have been used by Professor Dewar and me in our researches. For the method of fluorescence we have used a modification of Soret's eye-piece, substituting for the uranium glass-plate a wedge-shaped vessel full of a solution of æsculine, placed with its edge horizontal so that we look down on the fluorescent liquid. The wedge form of the vessel has the advantage of refracting out of the line of vision all the rays except those which produce

fluorescence, a matter of no small importance when light is to be observed (see Fig. 1).

Now, although the intensity of the sun's rays falls away rapidly beyond the Fraunhofer line H, and comes to nothing about as far above H as F is below it, it is far otherwise with the radiation of our terrestrial elements when heated up in the electric spark or arc, or even in some cases in flames; some of those elements which we know to be abundant in the sun, such as iron and magnesium, exhibit their most intense radiation, their strongest and most persistent rays, in the ultra-violet region, in waves which succeed one another at the shortest intervals. Indeed those metals so readily take up certain ultra-violet vibrations, that when there is much metal in the arc, and it is confined in a crucible of lime or magnesia, they often give their characteristic lines strongly reversed, dark absorption-bands being produced by the slightly cooled vapour which is outside the arc. This is seen in the photographic plate, Nos. 1 to 3. No. 2 shews the strongest magnesium line, in a region beyond the limit of the solar spectrum, at wave-length 2852, expanded and reversed. No. 1 shews it enormously expanded, its bright wings reversing iron lines up to S. No. 3 shews a strong group of iron lines, still more refrangible, also expanded and reversed by putting iron wire into the arc. The dark bands in the photograph are due to absorption by the metallic vapour, and in their places strong bright lines appear when less metal is present. The spectrum of iron is of all metals the most complicated, and those of the other elements which are most closely related to iron in chemical characters come next to it in the number and complication of their ultra-violet lines. Manganese and chromium are especially remarkable for shewing many groups of closely-set lines. No. 2 shews a group of chromium lines between the solar lines S and U. It is probably not without significance that this group of elements which exhibit the greatest variety in their chemical relations, and produce combinations of the greatest number of types, and the most complicated spectra, are also those which produce the most highly-coloured compounds. In marked contrast to the thick-set ranks of iron, manganese, and chromium lines, are the

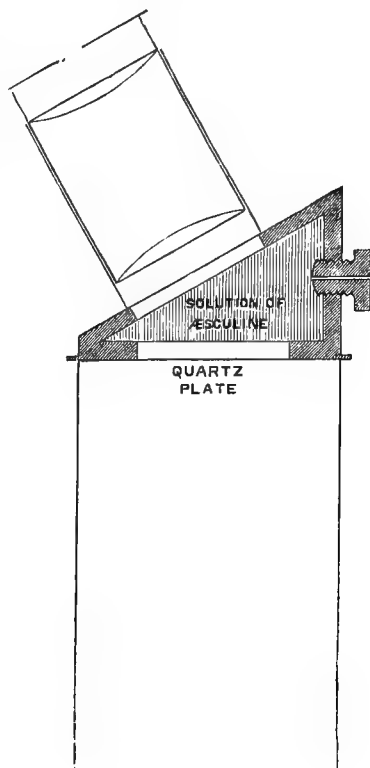


FIG. 1.

few scattered rays exhibited by those metals which form their combinations each chiefly on a single type, such as aluminium, and the alkali and alkaline earth metals. These spectra are probably even simpler than at first sight they seem to be. That of lithium is the simplest (Plate II, fig. 3): a series of single lines succeeding one another at decreasing intervals, and with diminishing intensity, closely resembling in these respects the spectrum of hydrogen. In the case of hydrogen, we know that the oscillation frequencies of some of its rays are related in a simple harmonic ratio. We are not able to say that the relation is so simple in the case of lithium; but still the whole series are probably overtones of a fundamental vibration, not so simply related as the harmonics of a uniform stretched string, but, like the overtones of a string which is not of uniform thickness, or is loaded at different points, similarly related in origin, though not exact harmonics. That the different rays are in many cases so related as overtones of a fundamental vibration appears more plainly, perhaps, when not single lines but groups of two, three, or four lines recur. Potassium shews a series of pairs to which the well-known violet pair, and perhaps that in the red also, belong. Calcium, magnesium, and zinc, each shew a series of triplets, which are alternately sharply defined and diffuse (see photographs 4 and 5 and Plate II, figs. 5 and 6). In other cases the same characters may be traced, though less readily, because there is sometimes more than one such series of lines or groups. The alkali metals have one such series in the visible spectrum, and another in the ultra-violet. It may happen in other cases that two or more such series overlap, and it may then be very difficult to distinguish and separate them.

In some cases elements shew at a lower temperature a far more complicated spectrum than they do at higher temperatures further removed from their points of liquefaction. This has been observed by Roscoe and Schuster in the case of the alkali metals potassium and sodium, which give at temperatures only a little above their boiling-points absorption spectra which consist of closely-set fine lines, producing an appearance of shaded bands quite unlike their emission spectra at higher temperatures. In some few cases we have observed similar "fluted" or "venetian blind" spectra, as they have been called, in the ultra-violet, as, for example, one produced by tin; but in general the temperature of the arc, which we have chiefly used in our observations on metals, is high enough to carry the metals beyond the stage in which their vibrations are constrained by the state approaching to liquefaction.

But though metals do not often shew spectra of this class at the high temperature of the arc, it is otherwise with metalloids and with compounds. Nitrogen gives in the arc as well as in the spark a channelled spectrum of singular beauty, extending with but short breaks almost to the extremity of the ultra-violet region which we have examined. (See photograph 7.) These multitudinous lines of nitrogen, constantly present in the arc taken in air,

help to make the problem of unravelling the spectrum of the arc, and assigning each line to its proper source, far more difficult than might at first be supposed. Carbon, which in the arc frequently gives a channelled spectrum in the visible region, gives only a limited number of lines in the ultra-violet; but cyanogen gives one set of flutings near the line L, and another near N, which are so brilliant in the arc as to obscure the metallic lines in their neighbourhood (photograph 4, between K and M and at N). To the same class we may refer the spectrum of water, of which the most brilliant portion is given in photograph 6.

The series of lines produced by the same element, which I have spoken of as overtones of a fundamental vibration, have been likened to these channelled spectra, but in reality they are very different. In the series, which I have supposed to have a sort of harmonic relation, the successive lines or groups of lines invariably become nearer to one another as the wave-lengths become shorter, and at the same time they diminish in strength and sharpness; whereas in the channelled spectra the strongest lines are at the end where they are most closely set, and they generally diminish in strength as they get further apart. Also increase of distance between the lines of channelled spectra is sometimes towards the less, sometimes towards the more, refrangible end of the spectrum.

I have before observed that a great part of the ultra-violet spectra of the elements which we have observed lies entirely beyond the limit of the solar spectrum; that limit is the line U at wave-length 2947. But though this is the limit of the solar radiation which reaches us on the earth, we can hardly suppose that the sun itself, or the photosphere, emits no radiation of shorter wave-length. We know that there is plenty of iron and magnesium in the sun, and the strongest radiations at high temperatures of these elements are of shorter wave-length than U. Moreover, the continuous spectra of incandescent solids in many cases extend far beyond U. The continuous spectrum of burning magnesium reaches quite up to the wave-length 2380, that of the flame of carbon disulphide mixed with hydrogen and fed with oxygen reaches even further, that of lime heated with an oxy-hydrogen blowpipe, though feeble beyond the limit of the solar spectrum, extends up to wave-length 2680. The temperature of the sun cannot be less than that of any of these sources of heat, so that we are forced to suppose that the radiation, more refrangible than U, which leaves the body of the sun, is stopped somewhere either in our atmosphere, or in planetary space, or in the atmosphere of the sun himself. Now Cornu has found that when the thickness of our atmosphere traversed by the sun's rays is diminished as much as possible by taking the sun at its greatest altitude, and making the observation from an elevated station (the Riffelberg), the solar spectrum only reaches to wave-length 2932, that is, only a very trifle beyond U. We must therefore suppose that the absorbent substance, whatever it be, is not in our atmosphere. The

same reason will lead us to reject the notion that the absorption can be due to matter in planetary space, for it is not easy to suppose that the gases which pervade that space in extreme tenuity can differ much from those in our atmosphere, because the earth in its annual course must pick them up whatever they are, and they must then diffuse into our atmosphere, and we must in time have them in a more condensed state in our atmosphere than in planetary space. The absorbent is therefore probably neither in our atmosphere nor in planetary space, and we must look for it in the solar atmosphere. When we notice how much of the radiation of our terrestrial elements is of shorter wave-length than the solar line U, we might almost fancy that the blotting out of the sun's light beyond that point is simply due to an increase in the number and breadth of the Fraunhofer lines. Indeed we have frequently observed the strong magnesium line, wave-length 2852,

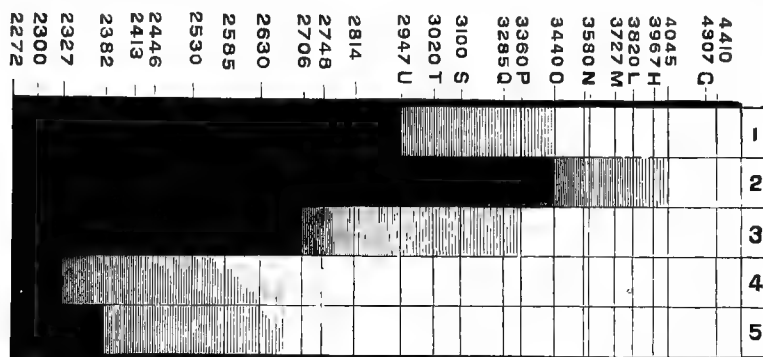


FIG. 2.

- No. 1. Solar spectrum.
- No. 2. Candle flame.
- No. 3. Lime light.
- No. 4. Carbon disulphide and hydrogen flame.
- No. 5. Magnesium flame.

expanded so that the dark absorption band in its middle reached quite up to U on one side (see photograph No. 1) and equally far on the other side, and this, together with such expansion of the strong iron lines beyond as we have occasionally observed, would go a long way towards completely hiding all light above U. But such expansions of iron and magnesium lines, high in the scale of refrangibility, do not occur without a considerable expansion of the lines of the same elements lower in the scale, expansions far exceeding what we actually observe in the Fraunhofer lines. Moreover the Fraunhofer lines, though dark by comparison with the brightness of the photosphere, are themselves luminous, even bright, when there is no other still brighter light wherewith to contrast them, so that if there were no other absorbent action the solar spectrum would be continued by the emitted rays of the metallic vapours which produce these lines. Probably then the absorbent

is something at a lower temperature, higher in the solar atmosphere. A change of temperature may, and in some cases certainly does, imply such a change of state that there may be a corresponding change in the particular vibrations which can be most easily taken up.

The metals in the liquid and solid states are so very opaque that we should hardly be able to discern their absorption spectra; nevertheless in very thin films they are translucent in different degrees. Gold leaf, as is well-known, transmits a green light, and we have found that a thin film of gold chemically deposited on a plate of quartz is fairly transparent for all the ultra-violet rays so that its selective absorption is almost wholly of the less refrangible rays. Silver deposited in a similar way produces a very different effect. It is almost wholly opaque, except for one rather narrow band which begins a little below the solar line P and extends with diminishing transparency to about S. Cornu has before noticed this property of silver, but placed the transparent band at wave-length 270 instead of 330. Dr W. A. Miller had observed that the light reflected by gold is equally distributed all through the ultra-violet, but feebler than that reflected by other metals; while that reflected by silver is characterised by giving a sudden cessation of the photographic image for a certain distance. These characters of the reflected rays he attributed to absorption by the metal.

When we examine the absorption produced by the haloid elements, we find that chlorine absorbs a wide band in the ultra-violet with its centre near the solar line P, extending, when the chlorine is in small quantity, from N to T, increasing in width on both sides when the quantity of chlorine is increased, but still leaving the rays above wave-length 2550 unabsorbed.

Bromine vapour shews an absorption band which begins in the visible spectrum, and extends, when the bromine is in small quantity, up to L, and when the bromine is in greater quantity up to P. From that point, up to about wave-length 2500, the vapour is transparent, but beyond it is again absorbent, the absorption increasing gradually with the refrangibility of the rays.

Iodine vapour, when thin, is transparent for ultra-violet rays, but produces strong absorption in the violet region. With thicker vapour this absorption extends nearly to H, but the vapour is still transparent for rays more refrangible than H.

Lecoq de Boisbaudran has observed that in the spectra of similar elements we may trace a shifting of similar lines, or groups of lines, towards the less refrangible side as the atomic weight is increased. Thus the violet pair of lines given by potassium is represented by an indigo pair in the case of rubidium, and a blue pair in the case of cæsium; and the indigo line of calcium is represented by a blue line in the spectrum of strontium, and by a green line in the spectrum of barium.

We may observe something of the same kind in regard to the haloid elements: the absorption band which in the case of the element of lowest atomic weight, namely chlorine, is altogether ultra-violet, is shifted towards the less refrangible side in the case of bromine, and lies altogether in the visible region in the case of iodine, the element of highest atomic weight.

It is remarkable that bromine in the liquid state and iodine in solution shew absorptions quite different from those of their vapours. A thin film of liquid bromine between two quartz plates is transparent for a band which ends just where the transparency of the vapour begins, while the film is opaque for rays both above and below this band. Iodine dissolved in carbon

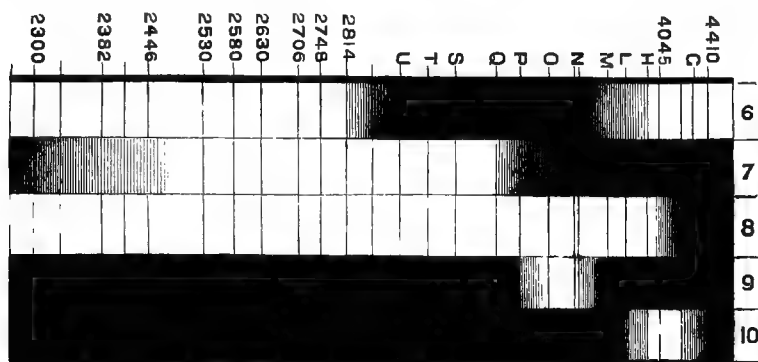


FIG. 3.

No. 6.	Absorption of chlorine.
No. 7.	" " bromine vapour.
No. 8.	" " iodine vapour.
No. 9.	" " bromine liquid.
No. 10.	" " iodine solution.

disulphide is also transparent for a certain distance, but the band is shifted to a less refrangible region lying between G and H.

Compound gases and vapours shew, as might be expected, various absorptions of ultra-violet rays. The absorbent action of coal-gas begins at about the wave-length 2680, and above 2580 it is nearly complete. Sulphurous acid has an absorption band extending from about R (3179) to rays of wave-length 2630, with a weaker absorption extending some way beyond these limits on both sides. Sulphuretted hydrogen produces a pretty complete obliteration of all rays above wave-length 2580. Vapour of carbon disulphide in very small quantity produces an absorption extending from P to T, shading away at each end. With more vapour this band widens, and a second absorption band begins at about the wave-length 2580. Chlorine peroxide gives a succession of nine shaded bands at nearly equal intervals between M and S, while in the highest regions of the spectrum it seems to be quite transparent.

I mentioned at the outset the probable connection between the intensity of the solar radiation and the sensitiveness of our eyes to rays of different colours. The consideration of ultra-violet absorption spectra leads to the mention of another fact connected with vision, or rather with the construction of the eyes of the higher animals. Soret has investigated, and recently Chardonnet has more fully examined, the limits of transparency of the crystalline, cornea, and vitreous humour of the eyes of various animals and man, and found them all more or less transparent for ultra-violet rays. The limit of transparency in many cases approaches, but never exceeds, the limit of the solar spectrum. Chardonnet places the limit of transparency of the crystalline of the human eye as low as M, which is not consistent with the observations of Herschel and Helmholtz before mentioned, but this inconsistency is probably due to alterations which had taken place after death in the eyes experimented on by Chardonnet. That the transparency of the materials of the eye does not extend beyond the solar line U, Chardonnet regards as a provision of nature to protect the retina from the extreme radiations of artificial lights; but I venture to offer a different explanation, which is, that the selection of the materials of the eye has been determined not by what they will absorb but by what they will transmit. If the materials in question were in any great degree opaque to the ultra-violet solar rays, these rays must be absorbed and must either be used in heating the absorbent or do work upon it in some form, perhaps alter it chemically, and so impair its efficiency as part of an optical instrument. I see, then, in the selection of these materials for our eyes an instance, one amongst many, of the marvellous adaptation of our organisation to the natural, rather than to the artificial surroundings in which we are placed.

DESCRIPTION OF THE PLATES.

In the photographic plate:—

No. 1 shows an expansion of the magnesium line at wave-length 2852, while it is also so strongly reversed as to produce a complete obliteration of all the lines above U within the range of the photograph, while its bright wing reverses the iron lines near T.

No. 2 shows the same line at *b* much less expanded but still self-reversing. The lines at *a* are also magnesium lines, wave-lengths 2795 and 2801. Most of the lines between *b* and *S* are chromium lines.

No. 3 shows iron lines reversed by putting iron wire into the arc.

No. 4 shows calcium lines in recurring triplets; also the cyanogen bands between K and M and at N.

No. 5 shows three of the zinc triplets.

No. 6 is the brightest part of the ultra-violet spectrum of water.

No. 7 shows part of the channelled spectrum of nitrogen in the ultra-violet.

The lithographic plate gives the position of the ultra-violet lines of several metals to a scale of wave-lengths.



To follow p. 280 (1)

ON THE USE OF A COLLIMATING EYE-PIECE IN SPECTROSCOPY

[*Proceedings of the Cambridge Philosophical Society*, Vol. iv. Pt. vi. (1883),
pp. 336 sqq.]

WE seem to owe to von Littrow the first suggestion for a spectroscope with only one telescope which should serve at once both as collimator and observing telescope; but hitherto for the most part such instruments have been abandoned on account of the embarrassment caused by reflexions from the surfaces of the object-glass. Professor Brackett (*American Journal of Science*, July, 1882) mentions such an instrument constructed for the College at Princeton, and says that it was necessary to put a patch on the object-glass to intercept reflected light, although it had been specially constructed with curvatures calculated to reduce the inconvenient reflexions to a minimum.

Professor Mendenhall, in the Memoirs of the Science department of the University of Tokio, Japan, has called attention to the advantages of a collimating eye-piece in grating spectroscopes.

The most obvious of these are (1) the facility with which a reflecting grating can be adjusted so that its plane may be perpendicular to the axis of the collimator if it is to be used in that position; and (2) the facility with which the distance of the slit from the object-glass of the collimator may be adjusted so that the light may be incident on the grating in a parallel beam. This condition has to be fulfilled in order to obtain the best definition whenever the telescope and collimator are not symmetrically placed with reference to the grating, that is to say, if a reflecting grating is used, in all ordinary cases. He points out however that when the axes of the telescope and collimator are equally inclined to the normal plane of the grating, which corresponds to the case of a prism in the position of minimum deviation, the definition is not dependent on the exact parallelism of the incident beam. This position of telescope and collimator is obviously attainable, when a reflecting grating is used, only when they are either identical or placed one above the other in the same vertical plane. We have not met with any precise account of the Princeton instrument. A collimating eye-piece with a plate of glass, or quartz, as reflector, while allowing the collimator and

telescope to be absolutely identical, has the disadvantage of much loss of light, and we preferred to make the axes of collimator and telescope slightly inclined to one another in the same vertical plane, but at such a small angle that one object-glass and tube serves for both. We use in fact only the upper half of the slit for the admission of light, and reflect the return beam by a right-angled prism placed close to the slit just below the centre. The edges of this prism are of course short and its upper bounding plane passes through the axis of the tube of the telescope. The length of the sides is about $\frac{3}{4}$ inch in order to give a sufficiently large field of view. When the source of light is large enough to fill the whole of the upper half of the slit the prism intercepts part of the light which would otherwise fall on the lower part of the object-glass, but no practical inconvenience results from that. There is no loss of definition because there is lateral symmetry in the incidence of the light on the object-glass. A stop with a small hole is placed immediately behind the reflecting face (the hypotenuse) of the prism to intercept stray light from the edges of the slit which might otherwise reach the eye.

The reflexions from the surfaces of the object-glass we have found less embarrassing than other observers seem to have found them. One reason is that the tube is lined throughout with black velvet. We have long since found the necessity of this when observing either extremity of the spectrum, as ordinary blacking and stops will not prevent a good deal of stray light entering the eye. Another reason is that we use a single plano-convex quartz lens as object-glass, so that there are but two surfaces to reflect any light. The plane surface produces a well-defined image of the slit which can be very well seen when the eye-glass is removed. It is however a distant object and cannot be seen through the eye-glass at all. It is quite intercepted by a very small patch on the centre of the object-glass, but this is not really needed, for when a strong light is used the slit can be made narrow and the reflected light reduced. The curved surface of the object-glass disperses the light it reflects more than the plane surface, so that more of it is absorbed by the sides of the tube.

It is easy to throw a strong light into the slit in such a direction as to give very inconvenient reflexions, but the proper direction is as easily attained by means of a lens in front of the slit fitted into a tube which is a prolongation of the telescope tube. When the source of light is so placed that the image produced by the lens is just above the centre of the slit the best results are obtained.

Prisms may be used as well as gratings with the instrument if the train terminate with a half prism with its face silvered, and we have tried such a plan with success. The dispersion is of course double what it would be with the same prisms used in the ordinary way, as the light passes twice through

them. The light is however enfeebled though the dispersion is increased, and the gain in the use of prisms appears to be less than it is in the use of gratings where the only extra cause of loss of light is the reflecting prism which makes but a very trifling difference.

The advantages which we think we attain by this method are:—

1. Great dispersion without loss of definition.

The ordinary formula connecting the wave-length, grating space, and inclinations of the collimator and telescope to the normal is $a(\sin \theta + \sin \phi) = n\lambda$, where a is the space between successive lines of the grating, θ , ϕ the inclinations of the axes of the collimator and the telescope respectively to the normal, n the order, and λ the wave-length.

In ordinary instruments the difference between θ and ϕ must be something considerable, and for the spectra of the higher orders either the incident or the diffracted ray is very oblique and the brightness as well as the definition suffers. For any particular position of the grating with reference to the collimator the angular separation of two rays in the field of view will be measured by $d\phi/d\lambda$, which is proportional to $n \sec \phi$, and the maximum value of n is obtained by making both θ and ϕ as large as possible. It will therefore happen frequently, when both θ and ϕ can be made as near 90° as we please, that we are able to observe a particular ray in a spectrum of a higher order than when there must be a considerable difference between them. The definition is also as good as it can be made for any given grating because the eye-piece ensures the parallelism of the incident rays. As a test we may mention that with Rowland's grating having 14,438 lines to the inch the less refrangible of the E lines is very distinctly divided in the 5th order, though we were not able to resolve this line with a Rutherford grating having 17,296 lines to the inch used in the old way, notwithstanding that this latter grating is in some respects the better of the two. The E group in the 5th order bears the magnification of a Ramsden eye-piece, with lenses of one inch focal length, very well. This is the highest power we have used; and it will be seen that the magnification is independent of the object-glass of the telescope in this case. With the 6th order no more can be seen though the lines are wider apart. It will be observed that for a given inclination of the telescope to the normal the dispersion with the collimating eye-piece is just double what it is when there is a separate collimator placed normal to the grating, for in the former case we have $n\lambda = 2a \sin \phi$ and in the latter $m\lambda = a \sin \phi$, so that $n = 2m$. Against this we must set the disadvantage of the increased number of overlapping spectra, the most troublesome inconvenience attending the use of gratings. The uncorrected lenses which we use for the sake of observing the ultra-violet rays, are an advantage in regard to the overlapping spectra, because the parts of two spectra which are in the field of view at the same time are not in focus together. Thus if the image of

the sun, or other source of light, is projected on to the slit with a lens of short focus, the spectrum when in focus forms a narrow but bright band, whereas the overlapping spectrum which is out of focus forms a much broader and consequently less bright band. This weakening of the overlapping spectrum is sufficient when the brighter parts of the solar spectrum are under observation, but not sufficient when either extremity of the spectrum has to be observed against an overlapping bright part. In such cases we have used a coloured glass or liquid to cut off the brightest light. Where the spectrum is more discontinuous than that of the sun or electric arc the overlapping spectra are not so frequently in the way.

2. Facility and accuracy in measurement of wave-lengths.

The method of measuring wave-lengths commonly adopted, namely, to fix the grating perpendicular to the collimator and read the deviation of the ray in the corresponding orders of spectra on the two sides, leaves little to be desired in point of accuracy, inasmuch as the errors of adjustment affect the readings on the two sides in opposite ways and so are compensated in the result. By the use of the collimating eye-piece equal accuracy is obtained by readings on one side only. This is owing in the first place to the facility and accuracy with which the zero reading is obtained. The collimator being fixed and the grating moved the zero reading is taken by placing the grating so that the image of the slit formed by direct reflexion from the grating may be on the pointer or cross wires in the eye-piece. The readings of the ray to be measured may then be taken in the successive orders of spectra one after another. In the next place there are no instrumental errors of adjustment to be taken into account. It does not matter if the axis of the collimator or the plane of the grating do not pass accurately through the centre of rotation. All that is required is the angle through which the grating is turned, that is to say the circle must be well divided. Readings on the two sides may still be taken and will help to eliminate errors of reading and errors due to inequalities of temperature and so on. For a given angular deviation the dispersion is double what it is in the old method which facilitates accurate reading; and it often happens that a spectrum can be observed of an order which involves a deviation greater than any which can be observed in the old method. Thus with a grating which when fixed perpendicular to the collimator will only shew the D lines in the first and second orders, it may be possible to observe them with a collimating eye-piece in the 5th order. Moreover gratings are usually very unequal on the two sides. The Rowland's grating we have used gives very feeble spectra in orders above the second on one side, bright spectra of those orders on the other side, and it is a great advantage to be able to use the bright side alone. By way of example of the accuracy easily obtainable by the use of the collimating eye-piece we may cite one determination. Readings were taken of the *b* group of magnesium lines in the 3rd, 4th, and 5th orders on

both sides, that is six observations of each line, the circle being divided in 10' and the vernier reading half-minutes. The mean of the two readings of the same line in the same order on the two sides did not in any case differ from the single reading by half a minute. The wave-lengths deduced from the whole set were

	b_1	b_2	b_4
	5183·14	5172·20	5166·62
Ångström's Nos.	5183·10	5172·16	5166·88

In comparing our numbers with those of Ångström it was of course necessary to determine the distance between the lines of the grating according to the standard of length employed by Ångström. This was done by observations of the deviations of the D and E lines in the spectra of a sodium flame and of a spark between iron points respectively, as well as in the solar spectrum. For spectroscopic purposes it appears to us to be far the best plan to adopt Ångström's standard of length, whether his millimetre be the most accurate attainable or not, and when we get a more exact determination of absolute wave-length, all numbers on Ångström's scale can be reduced to the new scale by multiplication into a constant factor. For the purpose of reducing the grating space to Ångström's scale Mendenhall has proposed the use of a rather feeble iron line below E, but it seems to us far better to use the mean of the two E lines, because this was Ångström's standard line on the measurement of which he bestowed the greatest pains; besides E_2 is a strong and easily recognised line in the spark spectrum of iron. The D lines are convenient from the facility with which they may be observed, and though they are diffuse lines in the sodium flame they can be read accurately by the reversed line when the dispersion is high. The temperature correction is an important one whenever the observations are carried on in a place of variable temperature, a change of 4° in the temperature of the Rowland's grating we have used making a difference of more than half a minute in the deviation of the b group in the 3rd order. Mendenhall has determined the coefficient of expansion of one of his gratings by observations of the deviation at different temperatures, and his result agrees very nearly with the coefficient of expansion of speculum metal observed by Smeaton; and it is sufficient, with our present instrumental means, to correct the grating space for temperature by either coefficient.

It had occurred to us that instead of measuring directly the angle through which the grating is turned we might measure the deviation of the ray reflected from its surface and so double the angle to be measured and diminish errors of measurement. This method, however, does not answer so well as the other when the measures are taken on one side only, and the reasons are obvious. If the two telescopes are not very accurately adjusted to the centre of rotation sensible errors will affect the measured angles; and

the zero reading cannot be obtained in the same way as the other readings but has to be found by placing the telescope opposite the collimator and taking the reading in that position. The method answers well if the readings are taken on both sides. The adjustment of the axis of the telescope to the centre is a troublesome business, and is liable to small but sensible errors in change of focus for the observation of different rays. We make the adjustment by first replacing the object-glass by a lens of short focal length so as to make the telescope into a microscope. A small plumb-line consisting of a single thread of unspun silk is then adjusted on the top of the instrument until it does not alter its place in the field of view when the turn-table or the telescope is rotated. The cross wires of telescope and collimator are then brought on to it. After this has been done the readings on the two sides differ so much that the double readings cannot be dispensed with. By taking the mean of the readings on the two sides very accurate results may be obtained, as both instrumental errors and errors of reading are reduced as much as possible. Thus three readings of the D lines on each side, with a Rowland's grating on which the distance between the lines had been gauged by readings of the solar lines E, gave the wave-lengths 5895·06 and 5889·05, numbers which differ from Ångström's by only '07.

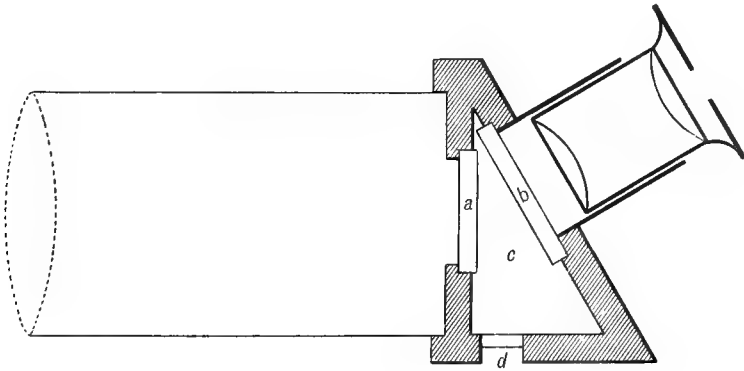
In order to photograph lines for the purpose of wave-length measurement, we have a small photographic slide which holds a plate one inch long by half an inch wide. When in use this slide takes the place of that portion of the instrument which carries the pointer and eye-lenses. A sliding shutter exposes only the lower half of the plate which is exactly opposite the reflecting prism, and when the exposure of that half of the plate is completed, the plate which is held in a small drum is revolved through 180° about an axis perpendicular to its plane, and thus what was before the upper side becomes the lower. The second half of the plate is now exposed and thus two images of the line are impressed on the plate at equal distances on either side of the axis about which the plate was turned. This axis in fact takes the place of the cross wires or pointer as the point of reference; and the distance of the line from it has to be deduced from the distance between the two images of the line measured under a microscope by a micrometer, and has then to be reduced to arc and added or subtracted from the observed angle of inclination of the grating. Two sets of photographs of the strong magnesium line taken in this way gave the wave-lengths 2851·9 and 2851·7 respectively; the wave-length found by the old method being 2852·0. This line is always diffuse, so there is room for some error in the determination of its middle.

The eye-piece was constructed for us by Mr A. Hilger, who carried out our instructions very carefully.

ON SOME MODIFICATIONS OF SORET'S FLUORESCENT EYE-PIECE

[*Proceedings of the Cambridge Philosophical Society*,
Vol. iv. Pt. vi. (1883), p. 342]

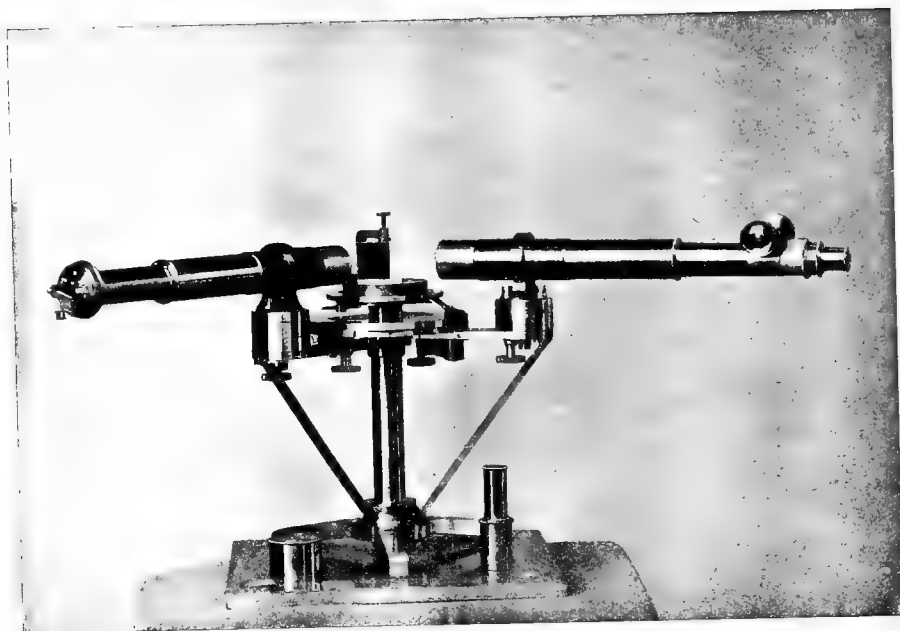
IF the eye-piece of the spectroscope be removed and a plate of uranium glass substituted there is no difficulty in seeing, in a dark room, the brightest ultra-violet lines by the fluorescence, and approximate measures of the deviation of them may of course be made. But as soon as you bring an eye-glass to bear on the image and try to take exact measures it becomes very tiresome. All extraneous light has to be excluded, and unless the slit is very wide the fluorescent light is in most cases so faint that it is barely possible to see the pointer without losing sight of the line to be observed.



In Soret's eye-piece the eye-glass is moveable about a vertical axis so that the fluorescent plate can be viewed obliquely from one side and so stray light coming down the tube of the telescope does not reach the eye. It occurred to us that it would be better to look down on the fluorescent plate obliquely from above. The spectrum and pointer would then be foreshortened in a vertical plane only and observation facilitated. Further, if the fluorescent screen were in form of a prism of small angle with one face perpendicular to the axis of the telescope and the other perpendicular to

the axis of the eye-lenses, the best conditions would be secured for seeing the fluorescent light while stray light would be refracted out of the line of vision. Eye-pieces on this plan have accordingly been made for us by Hilger, one with a thin wedge of uranium glass and others with a wedge-shaped vessel of which the side next the object-glass is a plate of quartz, and on the inner face of this the pointer is placed. The side of the vessel next the eye-lenses is of glass, and the vessel is filled with a solution of *æsculine* made slightly alkaline with ammonia. The body of the vessel is of brass, and there is a small window closed with glass at the bottom through which light may be thrown on the pointer when necessary.

The figure shews the eye-piece in section. *a* is the quartz plate, *b* a glass plate, *d* the window closed with glass, *c* the hollow which is filled with *æsculine* solution through a hole at the side which is closed with a screw plug with a minute perforation. The eye-lenses must be adjusted to the proper distance for distinct vision of the inner face of *a* before the eye-piece is inserted into the telescope.



To face p. 289

ON A SPECTROMETER AND UNIVERSAL GONIOMETER ADAPTED
TO THE ORDINARY WANTS OF A LABORATORY

[*Proceedings of the Cambridge Philosophical Society*, Vol. iv. Pt. vi.
(1883), p. 343]

THE instrument exhibited to the Society was designed for use as a spectroscope, for the measurement of refractive indices and generally for all purposes in which angular measurements are required. Its chief features are first the steady support given to the telescopes by the peculiar form of the brackets which carry them. Each bracket has a vernier, and the telescopes can be brought up to one another as close as the diameters of the object-glasses will allow. Above the circle is a turn-table provided with a vernier which can be moved through the whole 360° without interfering with the telescopes, so that the angular motion of any object upon it can be read while the telescopes are fixed. It can be used as a repeating circle if desired. There are adjustments for level of the telescopes and they can each be rotated in azimuth on their brackets when it is required to use them with a combination of prisms.

The instrument is provided with a prism with three polished faces giving refracting angles of 45° , 60° or 75° at pleasure and good definition in each position. The same prism can be used as a "half-prism" by placing its short face nearly perpendicular to the axis of the collimator, when the light will undergo internal reflexion at the next face and be dispersed at emergence from the third face. In this position of the prism the telescope and collimator are parallel and nearly in the same straight line, so that the instrument can be used as a direct vision spectroscope which is sometimes useful.

The instrument has been well constructed by A. Hilger, of Stanhope Street, London, N.W., and is shewn in the photograph opposite.

ON SUN-SPOTS AND TERRESTRIAL ELEMENTS IN THE SUN

[*Philosophical Magazine*, Series 5, Vol. xvi. (1883), pp. 401 sqq.]

THE publication of spectroscopic observations upon sun-spots made at Greenwich places within our reach a gradually increasing body of facts bearing on solar chemistry; and though we have not made a special study of sun-spots, yet the points of contact between the appearances presented in sun-spots and those observed by us in the spectra of terrestrial substances are so many, that we think some discussion of them will be of interest.

The spectroscopic appearances of sun-spots in general point, as all, we believe, are agreed, to the conclusion that in a spot we are looking through an unusual depth of the solar atmosphere charged with metallic and other vapours: that for some reason there is at a spot a depression in the general contour of the photospheric clouds, so that the light which reaches us from the spot has come to us from a greater depth in the sun and been filtered through a greater thickness of absorbent gaseous matter. The depression in the photospheric cloud may be the result of some of the violent atmospheric motions which are frequent in the sun, moving the clouds about and causing a downrush at the spot; or it may be the result of an ascending current of vapour at a temperature higher than the mean temperature of the photosphere, which converts the clouds into the gaseous condition, as sunshine dissipates the aqueous clouds in our atmosphere. If the spot is due only to a downrush of the upper atmosphere of the sun, we should be merely looking through a greater quantity of the outer atmosphere, increased in density and in temperature but consisting mainly of the same materials as before, and driving the photosphere, the chief source of light, downwards. We should expect to see the ordinary absorption-lines strengthened, and perhaps some new lines, due to a higher temperature, developed. For we must remember that a vapour is capable of absorbing the same kind of radiation as it emits; and that as its emission-spectrum varies with change of circumstances, of which temperature is one, its absorption will vary too. If the clouds of the photosphere were not merely mechanically depressed, but partly vaporized at the spot, we should expect to see new absorption-lines; not only on account of the higher temperature of the vapours previously existing as such, but

because matter which had before been cloud, and emitted a continuous spectrum, had now become gaseous, with a discontinuous spectrum.

And here we would say a word about an *à priori* objection to the supposition that a spot may be a region of a temperature generally equal to, or even higher than, that of the photosphere at the same level. Messrs De La Rue, Stewart, and Loewy, in their *Researches on Solar Physics* (1st Ser. p. 31), have argued, very cautiously and in a questioning manner, from the known laws of radiation and absorption, that we must be looking through a stratum of atmosphere at the spot cooler than the photosphere, because from such a thickness of matter as the sun we must at all points get the total radiation due to the temperature. We do not at all question the general principle of this argument, but we question its application in this case, because the total radiation is not the same thing as the luminosity. There may be more radiation on the whole from the darker spot than from the brighter photosphere, if the excess be in the ultra-violet or the infra-red. It is a general rule with solids that the radiations of short wave-length increase with the temperature more rapidly than those of longer wave-length; and some of the terrestrial elements which are abundant in the sun, such as iron and magnesium, have an emission-spectrum which appears to be much stronger in the ultra-violet than in the visible region. The substance we call iron, whether it be one element or many, emits in the electric arc ultra-violet rays which are extraordinary both in number and intensity. We are not in a position to test whether the total radiation from a spot is as great as from an equal portion of the photosphere, because all the radiation more refrangible than the solar line U is cut off, before it reaches us, by some absorbent medium. There is, however, one argument which makes strongly for the supposition that the spot is a region of a temperature generally not lower than that of the rest of the photosphere, which is this: If we suppose the photosphere to be of the nature of clouds formed by condensation of metallic and other vapours in the sun's atmosphere, then the gaseous part of that atmosphere will be saturated with the vapour of the matters forming the cloud, and any depression of its temperature must cause a fresh formation of cloud, which would tend to destroy the character of a spot. Indeed an apparent dissolution of photospheric matter carried into spots has frequently been observed, according to Secchi, and seems to suggest an evaporation of the cloudy matter in the spot.

Dismissing, then, the *à priori* argument for the coolness of the spot in comparison with the photosphere as insufficient, and likely to encumber us in the interpretation of the observed facts, let us come to the recorded phenomena.

There is, first, the widening of the Fraunhofer lines. This is observed in all spots, but the lines are by no means all widened or all equally widened.

The diagram opposite p. 296 represents the lines in two spots (taken as samples) observed at Greenwich (Obs. 1881) to be widened. The range observed is from F to *b*, and the length of the lines drawn under the corresponding lines in Ångström's map indicates the amount of widening, except where the widening is excessive, when the actual breadth is given as it appeared. As to the precise cause of the widening of spectral lines, physicists are not agreed; but as a fact we know that increased density of the emitting vapour is directly or indirectly a cause of the widening of the spectral lines of terrestrial elements; and we may reasonably attribute the widening in the spots to the increased thickness of the solar atmosphere, denser of course in the lower part, through which the light comes to us. But, then, why are not all the Fraunhofer lines widened? and why are those that are widened so unequally widened? Whatever the cause be, similar phenomena are observed in the emission-spectra of terrestrial elements. In the first place, the lines of some metals are much more readily expanded than those of others. The ready expansibility of the lines of hydrogen and of the D lines of sodium is well known; while the lines of iron and titanium are much less easily expanded, but are nevertheless very sensibly enlarged when the electric arc is freely supplied with the metal. But even so some lines expand more than others. This is well seen in the case of magnesium, which has one ultra-violet line (wave-length 2852) which is far more easily expanded than any other of its lines. And for a large number of metals, when heated in the arc, we have observed that lines, or groups of lines, repeat themselves at intervals, and that of such series the alternate members are far more readily expanded than the others. This is the case with the doublets of the visible spectrum of sodium—which are alternately diffuse and sharp, the diffuse lines being more easily expansible—and with the triplets of the magnesium, calcium, and zinc spectra. In more complicated spectra it is very probable that the same thing occurs, but, from overlapping of the groups, the alternations are not so easily detected. At any rate, they exhibit some lines which are more easily expanded than others.

It is only necessary to watch with a spectroscope of sufficient dispersive power the spectrum of the arc while iron and other metals are fed into it, in order to see the great expansion of some lines and the comparative inexpandibility of others. Any theory which is to account satisfactorily for the expansion of lines must account for the difference in the amount of expansion of the different lines of the same substance, as well as for the fact, noticed in several cases, that lines do not all expand symmetrically (some spread out more on one side than on the other), and also for absorption-lines expanding as well as the emission-lines, and for the fact that the tension of the vapour has more to do with the expansion of the lines than its temperature has. We do not know enough about the mechanical nature of the collisions, as they are called, between the particles of a gas, whereby the motion of translation due to temperature is supposed to be converted into vibratory motions

producing radiation, to say whether in a gas of high density the frequency of the collisions between similar vibrating particles may not affect the period of some of their vibrations much more than that of others.

When we come to examine what lines are usually seen expanded in sun-spots, we see that a large number are those of iron; and besides these the lines of magnesium, calcium, barium, sodium, titanium, and nickel are frequently enlarged. In fact the greater part of the lines of all these elements are more or less enlarged in most of the spots observed at Greenwich in 1881. The hydrogen lines are sometimes enlarged, sometimes not. There may be, probably are, great variations of pressure in the region of a spot; and as it is not very likely that the material of the photospheric cloud contains hydrogen, the tension of the hydrogen in the solar atmosphere will not be increased by the evaporation of the cloud. Hence the variations in the density of the hydrogen will be chiefly due to the currents; and the same remark will apply to all those substances which do not ordinarily exist in the condition of saturated vapour in the sun's atmosphere.

But not only are lines sometimes widened and sometimes not widened in spots, but sometimes lines usually seen as dark lines disappear, or appear as bright lines. This has been satisfactorily explained as the effect of ascending currents bearing vapours into the upper regions at such a high temperature that their emission is equal to or exceeds their absorption. In fact it is just those lines which have been observed as bright lines above the sun's limb in solar storms which are absent or are reversed in spots. There is still the question why some lines of such elements as iron and calcium should belong to the category of lines seen extending to considerable heights in the solar atmosphere while others do not so extend. We are inclined to the opinion that this appearance of certain lines at high elevations to the exclusion of others is dependent more on the tension of the vapour than on its temperature. Of course there is a relation between the tension of a vapour and its temperature, and this relation is by no means the same for saturated as it is for unsaturated vapour; and there may be unsaturated low-tension vapour at a very high temperature when but little of the material of the vapour is present, as well as saturated low-tension vapour at a low temperature. Now the distinction of long and short lines in the electric discharge, first introduced by Thalén, to which Mr Lockyer has since drawn more particular attention, corresponds, as he has noted, with difference in the density of the vapour; the short lines being seen only near the poles or in the central portion of the discharge, while the long lines extend further. We know but little about the temperatures of different parts of an electric discharge; but in this case temperature and density of vapour may very well go together. It is otherwise when one element is present in very small quantity, as in the alloys on which Mr Lockyer has experimented. He found that in alloys containing only a very small percentage of one metal, it was the long lines

of that metal which were persistent in the spectrum. Hence it seems conclusive that long lines are the lines of vapour of low tension rather than of low temperature; the lines corresponding to the vibrations which the particles take up most readily when they are in the most unfettered state, in their least complicated aggregations. The short lines will on this supposition correspond to vibrations either of more condensed particles, or to vibrations induced by the constrained condition of a dense gas. This view is in harmony with the fact that only the long lines usually appear in the higher regions of the sun's atmosphere where the temperature is high enough to make the hydrogen luminous, but where the pressure, if we may judge by the width of the lines, is certainly very low.

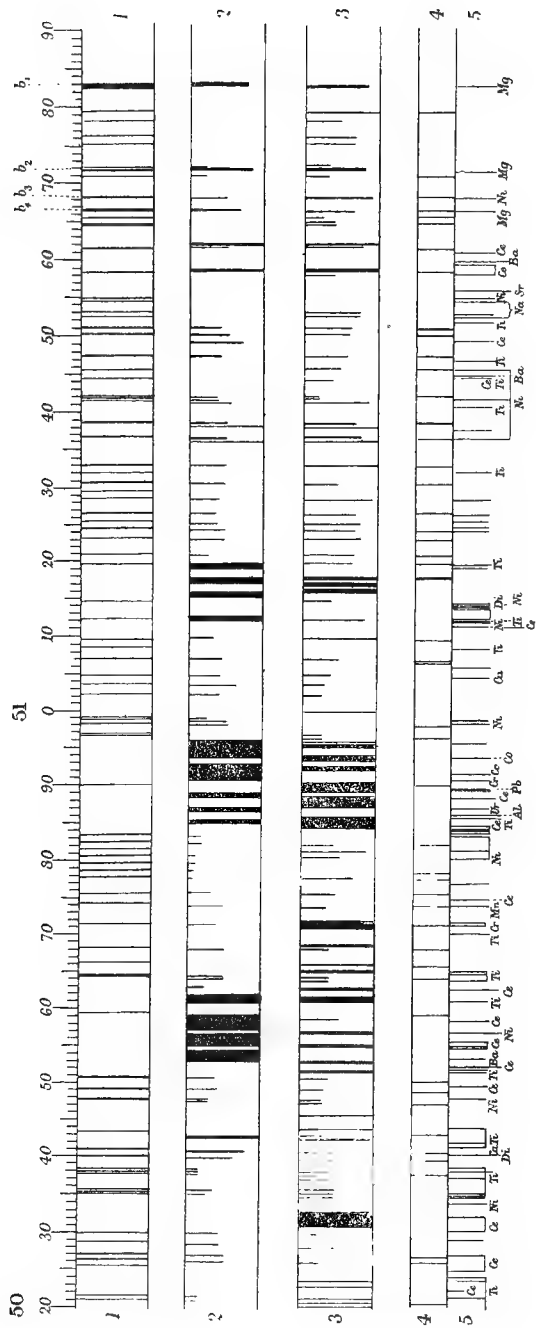
But besides the disappearance of some lines in some spots, new lines and bands frequently make their appearance. Now of the Fraunhofer lines only a fraction have as yet been identified as corresponding to lines of terrestrial elements; but we are inclined to the opinion that this is mainly due to the very imperfect examination which has as yet been made of the spectra of terrestrial substances. At any rate, we have found that it is only necessary to examine with high dispersive power any small section of the spectrum of the arc while different chemicals are dropped into it, in order to see a vast number of new lines develop themselves which have been hitherto unrecorded. The lowest horizon of the diagram shews the results of a somewhat hasty examination of the lines developed in this way by titanium and cerium, and in a few places by other substances. The titanium lines are permanent, but many of the cerium lines are evanescent: they come out strongly when fresh cerium is introduced, sometimes as broad bands, and quickly vanish as the cerium is dissipated, a few lines only remaining. The lines which remain are the lines of vapour of low tension, or long lines, while the others we suppose to be lines of vapour of high tension. It seems very probable, then, that if a careful examination were made of all the lines developed in the arc by all the known substances, most, if not all, of the Fraunhofer lines now ascribed to unknown substances would be accounted for. It is not a little remarkable that several of the most striking developments of lines observed at Greenwich in sun-spots closely correspond to new lines which we have observed to be given in the arc by cerium or titanium. In the case of cerium, the correspondence is so marked that it can hardly be accidental. Of course it is always easy to account for lines in the sun by the supposition of unknown elements brought up from the interior, or of unknown combinations or decompositions occurring under circumstances which we have not learned to imitate; but that is to cut the knot, not to untie it. When we consider the influence which circumstances besides temperature have on the vibrations which a given substance can assume, the comparatively partial way in which the spectra of our chemicals have been examined, the tendency of recent observations such as the artificial production of auroras with the characteristic

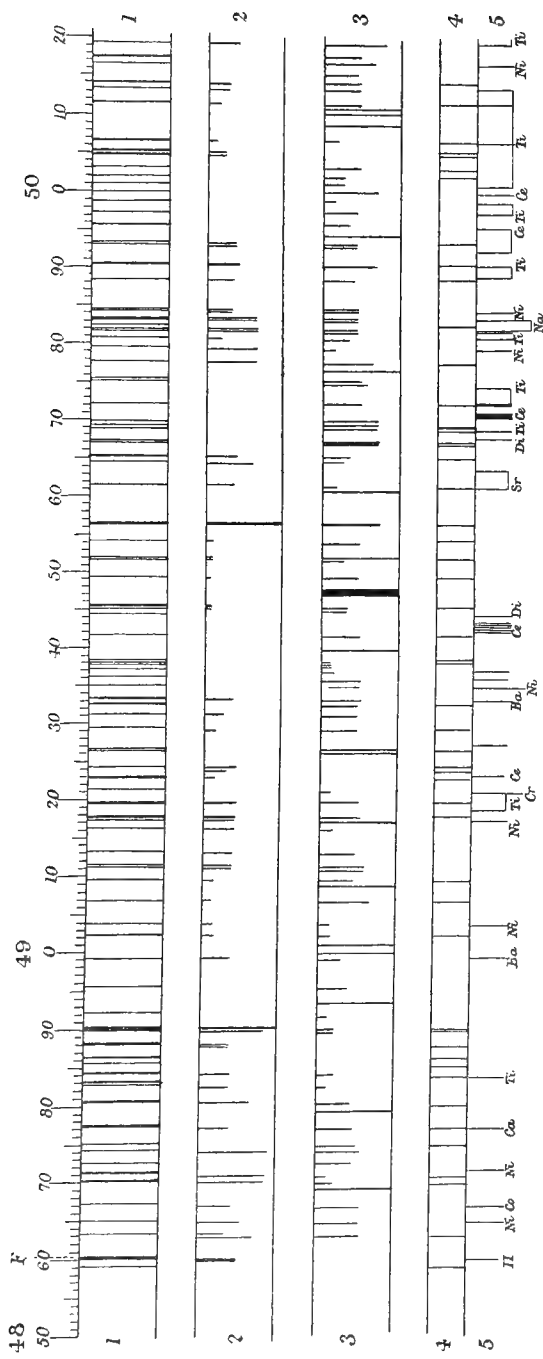
auroral line at no very great elevation in our atmosphere, and the identification by Egeroff of the groups A and B with the absorption of oxygen, we shall hesitate to say that there is ground for believing that the sun contains any thing which is not to be found on earth.

After all, there are very few of the lines developed in spots which do not appear at least as faint Fraunhofer lines in the ordinary solar spectrum. The maps of Fievez and Vogel give many such lines which are not in Ångström's map. Whenever lines of two metals are coincident, or nearly so, there is of course a double chance of increased width; and this corresponds with the observations. Further, it is noticed that the expansion of some lines is unsymmetrical—they expand more on one side than on the other. This may be an effect of the upward or downward motion of that portion of the vapour which is under observation; but it may also be due to the development of a second line close to that ordinarily seen. Such an effect we have observed in the case of the blue line of lithium, which appears to expand with increased tension of its vapour more on one side than on the other; but the effect is really due to the development of a second line close to the first and the expansion of both lines. This second line is seen as a narrow line as the metal is dissipated, and then disappears entirely long before the usual blue line shews any sign of failing. This will, we believe, satisfactorily account for some of the apparent motions of lines. Where a displacement, by reason of rapid motion of the sun's atmosphere, of some of the lines occurs without any displacement of others, we must suppose that the displaced lines are produced by one layer of the sun's atmosphere, while the undisplaced are due to another. This will account for the long lines, or lines of vapour of low tension, being displaced, while those due to vapour of high tension are unmoved, and *vice versa*. There is, however, one line which appears to be very anomalous in its behaviour, and requires further notice, because Mr Lockyer has more than once called special attention to it. This is the line with wave-length 4923. There is an iron line with this wave-length; but in iron it is certainly not a long line: it is not seen in the arc when there is only a very little iron present; and it comes out with increasing density of vapour. Corresponding with this character, it is frequently seen strengthened in spots like the other iron lines. On the other hand, a line of this wave-length is one of those most frequently (40 per cent.) observed by Young as a bright line high up in the solar atmosphere; and it has as frequently been observed by Tacchini in the spectrum of prominences. It should therefore be a long line, or one of vapour of low tension, if judged by this character; and this is confirmed by the fact recorded by Mr Lockyer that it is frequently absent from spots, which indicates that the emission in the upper regions balances the absorption. Moreover this line has (*Proc. R. S.*, xxxi, p. 349) been observed to be undisplaced in spots when the iron lines near it are displaced, shewing that the substance producing it is at a different

level from that producing the displaced lines. This is consistent with its existing in the upper regions to which only low-tension vapour of iron can reach. But as the line is certainly not a line of low-tension vapour of iron on earth, we are not justified in assuming it to be such in the sun; and we are driven to suppose it due to some unknown substance X* other than iron which at low tension has a line coincident, or nearly so, with a line of high-tension vapour of iron. Mr Lockyer thinks that the substance X is a constituent of terrestrial iron; but as the behaviour of the line in the sun does not correspond to the behaviour of the iron line on earth, the connexion between the two is reduced to the probable equality of wave-length. We suppose the tension of vapours in the upper part of the sun's atmosphere to be low as a general rule; but it may at times be locally higher, for solid matters falling into the sun and vaporized in its atmosphere may produce vapour of considerable tension until it has time to diffuse. The descent of dust from the region of the corona may thus produce lines at elevations where we should not otherwise expect to find them.

* Subsequently X was found to be helium.





No. 1 is part of Ångström's Normal Solar Spectrum.
 No. 2 gives the lines observed at Greenwich to be widened in Spot 436 and No. 3 those observed in Spot 614, the length of line representing the amount of widening, except when this was excessive when it is represented by the actual breadth drawn, Greenwich Obs. 1881.
 No. 4 gives the lines of Iron and No. 5 those of some other metals as observed in the Arc.

SPECTROSCOPIC STUDIES ON GASEOUS EXPLOSIONS. No. I

[*Proceedings of the Royal Society*, Vol. xxxvi. (1884), pp. 471 sqq.]

HAVING occasion to observe the spectrum of the flash of a mixture of hydrogen and oxygen fired in a Cavendish eudiometer, we were struck by the brightness, not only of the ubiquitous yellow sodium line, but of the blue calcium line and the orange and green bands of lime, as well as of other lines which were not identified. The eudiometer being at first clean and dry, the calcium must be derived either from the glass or from some spray of the water over which the gases with which the eudiometer was filled had been confined. It seemed incredible that the momentary flash should detach and light up lime from the glass, but subsequent observations have pointed to that conclusion. Our next experiments were made on the flash of the combining gases inclosed in an iron tube, half an inch in diameter and about 3 feet long, closed at one end with a plate of quartz, held in its place by a screw-cap and made tight by leaden washers. Two narrow brass tubes were brazed into the iron tube at right angles to the axis, one near each end, and one of these was connected with an air-pump, the other with the reservoir of gas. Into one of these brass tubes was cemented a piece of glass tube with a platinum wire fused into it, whereby the electric spark was passed to fire the gas.

The tube was placed so that its axis might be in line with the axis of the collimator of a spectroscope, and the flash observed as it travelled along the tube.

It was seen at once that more lines made their appearance in the iron tube than in the glass vessel, and one conspicuous line in the green was identified in position with the E line of the solar spectrum. Several other lines were identified with lines of iron by comparison with an electric spark between iron electrodes. There could be no doubt that the flash in an iron tube gave several of the spectral lines of iron. We supposed that this must be due to particles of oxide shaken off the iron by the explosion, and proceeded to try the effect of introducing various substances in fine powder, and compounds, such as oxalates, which would give fine powders by their

decomposition in the heat of the flame. Several interesting observations were made in this way. When some lithium carbonate was introduced, not only were the red, orange, and blue lines of lithium very brilliant, but the green line hardly less so. After the lithium had once been introduced into the tube, the lithium lines continued to make their appearance even after the tube had been repeatedly washed. When the lithium had been freshly put in, the red line was observed to be much expanded, very much broader than the line given by lithium in a Bunsen burner reflected into the slit for comparison. The light was dazzling unless the slit was very narrow; and it was noticed that if a spark by which the gas was fired was at the distant end of the tube, so that the flame travelled along the tube towards the slit, there was a reversal of the red line; a fine dark line was plainly visible in the middle of the band. When the spark was at the end of the tube next the slit, no reversal was, in general, seen. Later observations shewed that some other metallic lines might be reversed in this way, and photographs taken of the reversals. These observations with the eye on the reversal of the red lithium line were made with a diffraction grating, and were repeated many times. They shew that there are gradations of temperature in the flame, and that the front of the advancing wave of explosion is somewhat cooler than the following part. The combination of the gases is not so instantaneous that the maximum temperature is reached at once. When some magnesia was put into the tube the continuous spectrum was very bright, but the iron lines were still brighter. No line which could be identified as due to magnesium was observed with certainty; there was only a doubtful appearance of *b*. With sodium, potassium, and barium carbonates, only the lines usually seen when salts of those metals are introduced into a flame were noticed; but eye observations of this kind are extremely trying, on account of the suddenness of the flash and the shortness of its duration. Thallium gave the usual green line.

Subsequently we had the interior of the tube bored out so as to present a smooth bright surface of iron, and noted the iron lines which were conspicuous in the flash.

For the purpose of identification the pointer in the eye-piece was first placed on one of the strong iron lines given by the electric discharge between iron electrodes, and then, the discharge being stopped but the field sufficiently illuminated, the eye was fixed steadily on the pointer while the gas in the tube was exploded. In this way it was not difficult to see whether any given line was very bright in the flash. The lines thus identified were those having the wave-lengths about 5455, 5446, 5403, 5396, 5371, 5327, 5269 (E), 5167 (*b*₄). These lines were all many times observed in the way described, and as a rule were always present in the flash. Lines with wave-lengths about 5139 and 4352 were seen, and may possibly have been due to

iron, and several more lines were seen occasionally, but were not so regularly seen that they could be well identified. The lines $\lambda 4923$ and $\lambda 4919$ were specially looked for, but neither of them could be seen. A group of blue lines were noticed, and were afterwards identified by photography—a method much less trying than observations by eye. To give intensity to the photographs ten or twelve flashes were usually taken in succession without any shift of the instrument, so as to accumulate their effects in one photograph. For identification the spark between iron electrodes was also photographed, but with a shutter over the lower part of the slit, so that the image of the spark should occupy only the upper part of the field.

The following is the list of wave-lengths of the iron lines thus photographed:—

4414·7	3885	M 3727
4404·2	3877·4	3719·6
4382·8	3859·2	3709
4325·2	3849·7	3705·5
4307·2	3840·3	3647
4271·3	3833·6	3631
4250·5	3827·6	3618
4201·5	3825·2	3608·2
4143·1	L 3819·8	N 3580·5
4131·5	3815·3	3568·9
4071	3799·3	3564
4062·9	3795	3525·7
4045	3787	3496·8
4004·7	3766·6	3489·8
3967	3763·4	3476
3929·7	3757·7	3465·5
3927·2	3749·5	O 3440
3922	3747·2	
3920	3745·3	T 3019·8
3902·5	3736·5	
3898·4	3734·5	

As a rule no iron lines above O make their appearance; in a few plates T is visible, and it is possible that other lines may be obscured by the water spectrum, which always comes out and extends from near *s* to below R. Above T no line at all is visible in any of the photographs, though the spark lines come out strongly enough, and several of the strongest groups of iron lines, both of spark and arc lines, are in the region beyond T.

The spark by which the gas was fired passed in general between a platinum wire and the side of the small brass tube, and was out of view;

but in order to make quite sure that the lines were not due at all to the spark, the brass tube was lined with a tube of platinum foil which projected beyond the brass tube a short distance into the larger tube, and the spark passed between the platinum wire and the platinum tube. It was found that the same iron lines made their appearance in the flash whichever way the spark was passed.

Other experiments were made with explosions of carbonic oxide and oxygen, and with coal-gas and oxygen. The explosions of these gases were attended with much more continuous spectrum, and the metallic lines were not always as well developed as they were with hydrogen and oxygen, but on the whole there were as many metallic lines photographed from the flashes of carbonic oxide as from those of hydrogen. There is an uncertainty about the explosion of the carbonic oxide mixture which we cannot account for, even when we take into account the remarkable effects of relative dryness of the gas on the explosions discovered by Mr Dixon. Sometimes the explosions were so violent as to break the plate closing the end of the tube, though this had resisted the explosions of the hydrogen mixture, while at other times the wave of explosion passed slowly along the tube. The gas was in all cases confined over water and passed directly from the gasholder into the tube.

When the iron tube was lined with copper foil, only one copper line in the visible spectrum, $\lambda = 5104\cdot9$, was seen, and in the ultra-violet two lines, $\lambda 3272$ and $\lambda 3245\cdot5$. All three lines were very strong, and the two ultra-violet lines were in some cases reversed. These lines were also frequently developed when no copper lining was in the tube, probably from the brass of the small side tubes.

Copper also gave a line in the indigo, about $\lambda 4281$, decidedly less refrangible than the copper line, $\lambda 4275$, coincident apparently with the strong edge of one of the bands developed when a copper salt is held in a Bunsen burner.

A lining of copper which had been electroplated with nickel developed only one nickel line, $\lambda 5476$, in the visible part of the spectrum, but gave by photography the following lines in the ultra-violet:—

3807·5	3524	3445·5
3783	3514·7	3432
3775	3510	3422
? 3641	3492	3413·2
3618·3	3461·5	3391·5
3612·5	3457·7	3378·4
3597·3	3453	3369·6
3571·5	3451	3367·4
3565		

When nickel oxalate was put into the tube, lines with wave-lengths 3670·5, 3470·3 and 3389·6 in addition to the preceding were developed. It is doubtful whether the line λ 3451 be a nickel line. That at λ 3453 is ascribed to cobalt by Cornu, but it seems to be a nickel line as well.

When copper wire electroplated with cobalt was put into the tube, cobalt lines appeared with the approximate wave-lengths:—

4119	3594	3492 ?
4089	3568	3474
3995	3528	3462
3909	3525	3453
3894	3523	3431
3872	3502	3411
3845	3495	3404
3601		

The lines λ 3528 to 3523 form a continuous band in the photograph, so that these three lines may not represent the whole group at that spot. It is doubtful whether λ 3492 be a cobalt line as well as a nickel line.

No other metal gave anything like the number of lines that were given by iron, nickel, and cobalt.

A lining of lead gave the lines λ 4058, 3683·3 and 3639·3 strongly, and these lines were frequently developed, though less strongly, when there was no lead lining; the metal being without doubt derived from the leaden washers used to make the ends of the tube air-tight.

A strip of silver gave the lines λ 3381·5 and 3278, and these lines were sometimes reversed. No trace of the channelled spectrum of silver was developed even when silver oxalate was put into the tube, and furnished plenty of silver dust after the first explosion.

A magnesium wire about 2 millims. thick and two-thirds the length of the tube gave the *b* lines very well; that is to say b_1 and b_2 were well developed, and b_4 was also seen, but as the iron and magnesium components of b_4 are very close together, and the iron line had been observed before the introduction of the magnesium, it was not possible to say with certainty whether or not the magnesium line were present too. No other magnesium line could be detected. The blue flame line was carefully looked for, but could not be seen. The photographs shewed none of the magnesium triplets in the ultra-violet, nor any trace of the strong line λ 2852, which appears in the flame of burning magnesium, and is yet more conspicuous in the arc when that metal is present.

Metallic manganese, introduced into the tube in coarse powder, gave the group at wave-length about 4029 with much intensity, but no other

manganese line with certainty. In the visible part of the spectrum the channellings in the green due to the oxide were visible.

A lining of zinc produced no zinc line, and zinc-dust gave only a very doubtful photographic impression of the line λ 3342. A strip of cadmium gave no line of that metal either in the visible, or in the ultra-violet part of the spectrum.

Tin, aluminium, bismuth, and antimony also failed to produce a line of any of those substances, and so did mercury which was spread over copper foil made to line the tube.

Thallium spread as amalgam over the copper lining gave the lines λ 3775·6, 3528·3 and 3517·8.

Chromium was introduced as ammonium bichromate, which of course left the oxide after the first explosion. This gave the chromium lines with wave-lengths about 5208, 5205, 5204, 4289, 4274·5, 4253·5 very well and persistently, also the lines with wave-lengths about 3605, 3592·5, 3578·5.

Sodium salts (carbonate, chloride) developed the ultra-violet line λ 3301; and potassium salts gave the pair of lines about wave-length 3445; but no more refrangible line of either metal was depicted on the photographs. Lithium carbonate gave, besides the lines in the red, orange, green, and blue, the violet line, λ 4135·5; but no more refrangible line.

Photographs of a flame of mixed coal-gas and oxygen, in which an iron wire was burnt, shew, as might be expected, the same iron lines as are developed in the flash of the detonating gases, and of the same relative intensities. These intensities are not quite the same relatively as they are in the arc spectrum. Thus the lines λ 3859, 3745, 3737, 3735, and 3719 come out in great strength, much stronger than the lines λ 3647, 3631, 3618, which are remarkably strong in the arc.

German-silver wire, burnt in the flame of coal-gas and oxygen, gave the same nickel lines as were given by nickel in the detonating gases, as well as those of copper and lead.

Copper wire gave, besides the lines λ 3272, 3245·5, a set of bands in the blue, which correspond with those given by copper salts in flames, and are probably due to the oxide.

The greater part of the lines which we have observed in the flames of the exploding gases have been observed by us to be reversed when the several metals were introduced into the arc in a crucible of lime or magnesia; which is quite in accord with the supposition that the metals experimented on are volatile, and emit as well as absorb these particular rays, at temperatures lower than that of the arc.

That iron is volatile at a temperature below the fusing point of platinum, which is about 1700°C. , has been pointed out by Watts (*Phil. Mag.*, Vol. xlv, p. 86), who observed in the flame of a Bessemer converter almost all the green and blue lines of iron which we have seen in the exploding gases, besides one or two lines which we have not observed or identified. Having regard to this volatility of iron, it does not seem so surprising that iron lines should be observed accompanying those of hydrogen to great heights in the sun's atmosphere as that they should not be always seen there.

It is interesting to note that Copeland and Lohse (*Copernicus*, Dec. 1882) observed in the spectrum of the great Comet of 1882, amongst other lines, four lines, λ 5395, 5369, 5326, 5269, which are nearly identical with iron lines observed in the flash of the detonating gas.

It is remarkable that such volatile metals as mercury, zinc, and cadmium should give no lines in the flame of the exploding gases.

The gases exploded in the tube were generally mixed in nearly the proportions in which they combine chemically; but experiments were made with oxygen in excess, and also with hydrogen and carbonic oxide in excess. A small excess of any one of the gases did not seem sensibly to affect the result, but on the whole the metallic lines were more certainly developed when there was not much excess of oxygen, and more constantly developed when hydrogen was used than when carbonic oxide was used.

The absence of any metallic lines in the flame of the exploding gases which are more refrangible than T may be in part due to a falling off in the sensibility of the photographic plates for light of shorter wave-length; but as the spark lines of iron seem to be quite as strongly depicted on the plates in regions of the spectrum far above T as they are in the regions below, we think that want of sensitiveness in the plates cannot be the only reason for the absence of higher lines, but that the emissive power of the metals for these lines is feeble at the comparatively low temperature of the flame.

This supposition accords with what we have observed of the lines seen in a carbon tube heated by the electric arc (*supra*, p. 251). The iron lines photographed as reversed against the hot walls of such a tube were at certain stages of temperature the same, speaking generally, as those we have noticed in the flash of the detonating gases; but as the temperature of the carbon tube rose, more refrangible lines, including all the strong iron lines in the neighbourhood of T, the lines of aluminium near S, and the magnesium line λ 2852, were reversed in the photographs.

Gouy (*Comp. R.*, Vol. 84, 1877, p. 232), using a modification of Bunsen's burner fed with gas mixed with spray of metallic salts, observed at the point

of the inner green flame three or four iron lines which we have not observed in the flame of the detonating gas, the lines b_1 and b_2 of magnesium, two cobalt lines in the blue which we have not seen, one line of zinc, and one of cadmium, and the two strong green rays of silver. Can the appearance of these rays under these circumstances imply that the temperature of the inner green cone of a Bunsen burner, when the proportion of air to coal-gas is near the exploding point, is higher than that of the explosion of hydrogen and oxygen?

The interesting theoretical questions which are suggested by the facts recorded in this paper we must leave for future discussion.

THE TEMPERATURE OF SUN-SPOTS

[*Philosophical Magazine*, Ser. 5, Vol. xvii. (1884), pp. 302 sqq.]

PROFESSOR WIEDEMANN'S Note on our paper is very much to the point and deserves full discussion; but, admitting the truth of the principles on which he rests his argument, the conditions of the problem of solar spots do not seem to us so simple that those principles can be directly applied to it. We are not dealing with the radiation of a single body at different temperatures, but with the sum of the radiations and absorptions of a great thickness of more or less transparent material.

If we suppose the photosphere to consist of a cloud of liquid or solid particles giving a continuous spectrum, most of the radiation we get from those parts of the sun where there is no spot will be derived from this cloud, and we shall get scarcely any rays from the interior of the solar mass: the cloud will be comparatively opaque, its absorption corresponding generally to its emission. A further cooling of this cloud cannot well produce the phenomena of spots which are characterized by a selective absorption suggestive of a gaseous absorbent. Any cooling of the photospheric cloud, which must be surrounded by saturated vapour of its solid or liquid particles, would produce more solid or liquid with more continuous absorption. On the other hand, if the photospheric cloud were raised in temperature, so that the solid or liquid particles were to a considerable extent vaporized, we should then get radiation from the interior of the sun's mass, but sifted through the vaporized photospheric matter. The total radiation would, it is conceded, be greater now than before, but it would be made up of the radiation of the vaporized photosphere together with that of the sun beneath it. As regards the former part the radiating matter would be a gas instead of being solid or liquid, it would have changed its physical state and therewith the character of its spectrum. The radiation from the interior of the sun is added; but this arises from matter which may be different chemically, probably is different as to physical state, from the matter of the photospheric cloud. The argument of Prof. Wiedemann requires a continuity in the nature and in the state of the radiating matter; that is to say, it must be the same matter first and last, and it must not change from solid to gas. Neither condition is exactly fulfilled in the case before us. Let us suppose,

for the sake of definiteness, that the photosphere consists of particles of silicon, in the solid or liquid state, emitting a continuous spectrum; and that by some means it is further heated until it becomes gaseous, as we have it in the electric arc; it will now emit very little visible radiation but some very strong ultra-violet rays. The radiation from silicon in the visible part of the spectrum appears to be not relatively but absolutely less when it is gaseous than when it is solid. The whole argument of the gradual shortening of the period of oscillation with increase of temperature hangs on the supposition that there is a continuity of state, which must not be assumed to be the case in sun-spots. The phenomena of spots are those of increased absorption by (1) increase in the number of Fraunhofer lines, and (2) increase in their breadth or in their darkness. Now the increase in the number of Fraunhofer lines may be due either to an addition to the sun's atmosphere of the vapours of some substances not usually present, or to an increase in the rays absorbed by those which are usually present.

Increase of temperature frequently causes vapours to emit (and absorb) rays not seen at lower temperatures, and increase of temperature might add to the number of different gaseous substances in the sun's atmosphere by evaporating materials which had been before solid or liquid. On the other hand, cooling might allow of the formation of chemical compounds with absorptive powers quite different from those of their (separate) components. We cannot then safely infer either an increase or a decrease of temperature from an increase in the number of Fraunhofer lines. But, turning to the increased width of the lines, we know no case in which such an effect is produced by a diminution of temperature. Many examples seem to indicate that such widening is connected with increased density of the vapour producing the line; not however increased density produced by cooling, but only increased density produced by increased evaporation, increased (partial) pressure of the vapour. In fact, when a line is self-reversed (as it has been called) the dark line due to the cooler vapour is always narrower than the bright line emitted by the hotter vapour, even when there is no reason to think the hotter vapour to be more dense than the cooler, as in the case of the reversal of the F line of hydrogen when sparks are passed through hydrogen, as observed by Hasselberg ("Ueber die Spectra der Cometen," *Mém. de l'Acad. Imp. St Pétersbourg*, Ser. 7, Vol. xxviii, No. 2, p. 74 note) and by ourselves (*supra*, p. 267).

Any compression produced by a carrying downwards of the atmosphere must be attended with an increase of temperature. We have been driven by considerations of this kind to see whether the argument for the comparative coolness of spots based on the total radiation is irrefragable; and we have concluded that it is not, even after taking into account the considerations very properly adduced by Professor Wiedemann.

ON THE SPECTRAL LINES OF THE METALS DEVELOPED BY EXPLODING GASES

[*Philosophical Magazine*, Ser. 5, Vol. XVIII. (1884), pp. 161 sqq.]

NOT long since Berthelot published the results of some investigations, by means of a chronograph, of the rate of propagation of the explosion of mixtures of oxygen with hydrogen and other gases. He found that in a mixture of oxygen and hydrogen in the proportions in which they occur in water, the explosion progressed along a tube at the rate of 2841 metres per second; not far from the velocity of mean square for hydrogen particles, on the dynamic theory of gases, at a temperature of 2000° .

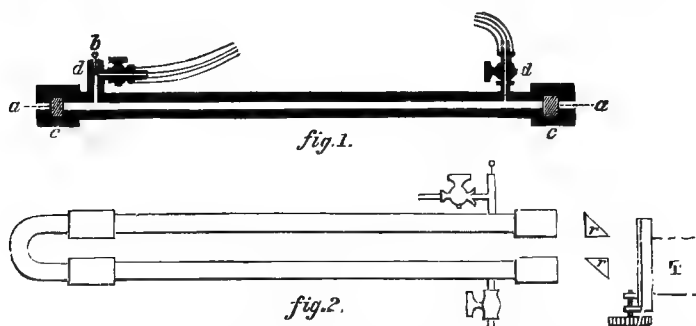
This is a velocity which, though very far short of the velocity of light, bears a ratio to it which cannot be called insensible. It is in fact about $\frac{1}{105000}$ part of it. Hence if the explosion were advancing towards the eye, the waves of light would proceed from a series of particles lit up in succession at this rate. This would be equivalent to a shortening of the wave-length of the light by about $\frac{1}{105000}$ part; and in the case of the yellow sodium lines would produce a shift of the lines towards the more refrangible side of the spectrum by a distance of about $\frac{1}{107}$ of the space between the two lines. It would require an instrument of very high dispersive power, and sharply defined lines, to make such a displacement appreciable. With lines of longer wave-length than the yellow sodium lines, the displacement would be proportionately greater. Further, if a receding explosion could be observed simultaneously with an advancing explosion, the relative shift of the line would be doubled, one image of the line observed being thrown as much towards the less refrangible side of its proper position as the other was thrown towards the more refrangible side. The two images of the red line of lithium would in this way be separated by a distance of about $\frac{1}{8}$ of a unit of Ångström's scale; a quantity quite appreciable, though much less than the distance between the components of b_3 , and about equal to the distance of the components of the less refrangible of the pair of lines E. We thought therefore that we might test theory by experiment.

A preliminary question had, however, to be answered. What lines could

be seen in the flash of the exploding gases? We were pretty certain that the hydrogen lines could not be seen, but that probably we might get sufficient dust of sodium compounds floating in the gas to make the sodium lines visible. A preliminary observation was made on the flash of mixed hydrogen and oxygen in a Cavendish's eudiometer, which shewed not only the yellow sodium lines, but the orange and green bands of lime and the indigo line of calcium all very brightly, as well as other lines not identified. The flash is very instantaneous, but nevertheless produces a strong impression on the eye; and by admitting the light of a flame into the spectroscope at the same time as that of the flash, the identity of the lines was established. That sodium should make itself seen was not surprising, but that the spectrum of lime should also be so bright had not been anticipated. At first we thought that some spray of the water over which the gases were confined must have found its way into the eudiometer; but subsequent observations led us rather to suppose that the lime was derived from the glass of the eudiometer. The lime-spectrum made its appearance when the eudiometer was quite clean and dry, and when the gases had been standing over water for a long time.

To obtain the high dispersion requisite, as already explained, we made use of one of Rowland's magnificent gratings, with a ruled surface of $3\frac{1}{8}$ by $2\frac{1}{8}$ inches, and the lines 14,438 to the inch. One telescope fitted with a collimating eye-piece served both as a collimator and observing telescope; and by this means we were able to use the spectra of the third and fourth orders with good effect.

Observations were made with this instrument on explosions in an iron tube shewn in section in fig. 1, half an inch in diameter, fitted at the end



with a thick glass plate (*a*), held on by a screw-cap (*c*) and made tight with leaden washers. Small lateral tubes (*d d*), at right angles to the main tube, were brazed into it near the two ends, for the purpose of connecting it with the air-pump, admitting the gases, and firing them. For this last purpose a platinum wire (*b*) fused into glass was cemented into the small tube, so that

an electric spark could be passed from the wire to the side of the small tube when the gases were to be exploded.

To bring out the lithium lines, a small quantity of lithium carbonate in fine powder was blown into the tube before the cap with glass plate was screwed on. Powder was used because we supposed that it must be loose dust which would be lighted up by the explosion. The lithium lines came out bright enough, and it was unnecessary to put in any more lithium for any number of explosions. The tube was of course quite wet after the first explosion from the water formed, but the lithium lines were none the less strong. Indeed, after the tube had been very thoroughly washed out, the lithium lines continued to be visible at each explosion, though less brightly than at first. A good deal of continuous spectrum accompanies the flash which, from the overlapping of spectra of different orders, makes observations difficult, so a screen of red glass was used to cut this off when the lithium red line was under observation. In any case, however, close observation of the flashes is very trying, from the suddenness with which the illumination appears and the briefness of its duration. At first we compared the lithium line given by the flash of the exploding gases with that produced by the flame of a small Bunsen burner in which a bead of fused lithium carbonate was held, both being in the field at once. While the flame-line was sharply defined, the flash-line had a different character and was always diffuse at the edges; so that it was not possible in this way to substantiate the minute difference of wave-length indicated by theory, though the flash-line certainly seemed a little the more refrangible of the two.

We then tried taking the explosion in a tube bent round so as to be returned upon itself, the two parts of the tube being parallel to each other, and the glass ends side by side (fig. 2). The axis of the collimator (T) was made to coincide with that of one limb of the tube, so that the flash in that limb was seen directly; and by means of two reflecting prisms (r, r) the light from the other limb was thrown into the slit, and the two images were seen simultaneously one above the other. As the gas was ignited from one end of the tube, the flash was seen receding in one limb, approaching in the other, so that the displacement of the two lines would be doubled. Still we were unable to substantiate any relative displacement of the lines on account of their breadth and diffuse character. By washing out the tube the breadth of the lines was considerably reduced, but they remained diffuse at the edges, and baffled any observation sufficiently accurate to establish a displacement. Certainly there appeared to be a very slight displacement, but it was not so definite that one could be sure of it.

These observations, however, led us to some other interesting results. In the first place, one of the two images of the lithium line almost always was reversed—that is, shewed a dark line down the middle. This was the

line given by the flash approaching the slit. The receding flash in the other limb of the tube gave as broad a bright line, but it had no dark line in its middle. This observation was made a great many times; and the fact of the reversal established independently in the case of some other metallic lines by means of photographs. These reversals shew that in the wave of explosion the temperature of the gases does not reach its maximum all at once; but the front of the wave is cooler than the part which follows and absorbs some of its radiation, while the rear of the wave does not produce the same effect. One would suppose that there must be cooler lithium vapour in the rear of the wave as well as in its front; but it is possible that the absorption produced by it extends over the whole width of the line, and not only over a narrow strip in the middle. For we observed that when a little lithium carbonate was freshly put into the tube, the red line was so much expanded as to fill the whole field of view—that is to say, it was some ten or twelve times as wide as the distance between the two yellow lines of sodium; but by washing out the tube with water (that is, by reducing the quantity of lithium present in the tube), the line could be reduced in width until it was no wider than one-tenth of the distance between the two sodium lines. This seems to prove that the breadth of the line is directly dependent on the amount of lithium present.

M. Fievez has, in a recent publication (*Bulletins de l'Académie royale de Belgique*, 3rd Ser., Vol. vii, p. 350), concluded, from observations on sodium, that the widening of the lines is solely due to elevation of temperature. The flash of the exploding gases cannot be raised in temperature by the presence of a minute quantity more of a lithium compound; so that in our case the widening cannot be ascribed to any thing but the increase in the quantity of lithium present, or to some consequence of that increase. It is not improbable that the amount of lithium vaporized in the front of the wave of explosion is less than in the following part, and hence the absorption line is not so wide as the bright line behind it, while in the rear of the wave the absorption extends over the whole width of the bright band, and so is not so easily noticed. Only twice amongst many observations was any reversal of the lithium line seen in the receding wave of explosion.

On observing the flash with a spectroscope of small dispersion instead of that with the grating, the continuous spectrum was very bright, but the metallic lines stood out still brighter; not only the red line of lithium, but the orange, the green, and the blue lines were very bright, and continued so when the pressure of the gases before explosion was reduced from one atmosphere to one-third of an atmosphere. The violet line was not seen, but it may have been so much expanded as to be lost in the continuous spectrum; for it shewed in a photograph afterwards taken. Other lines were, however, seen—the sodium yellow lines, the calcium indigo line, a group of other blue lines, and a group of green lines, amongst which one line was conspicuous,

and this line, by comparison with the solar spectrum, was identified with E. We had not expected to see any lines of iron, as iron and its compounds give no lines in the flame of a Bunsen burner, and we supposed that it would only be volatilized at a much higher temperature. But the appearance of E suggested that other of the green and blue lines might be due to iron; so we proceeded to compare the positions of these lines with those of the electric spark between iron electrodes. For this purpose one of the spark-lines was first brought carefully on to the pointer, or cross wires, in the eyepiece of the observing telescope, and then, the passage of the spark being stopped, the flash of the exploding gases was observed. It was not difficult to see whether any line was on the pointer; and the observation could be repeated as many times as was desired without any shift of the apparatus. Nine of the most conspicuous green and yellowish-green lines in the flash were thus identified with lines of iron. For the blue and violet we adopted the photographic method as much less trying to the eyesight. Eight to twelve flashes were taken in succession without any shift of the apparatus, so as to accumulate their effects on the photographic plate. Eight flashes were found enough in general to produce a good impression, and more than twelve could not well be taken without turning out the water which accumulated in the tube, and cleaning the glass which closed its end. After the flashes had been taken, but without shifting the photographic plate, the slit of the spectroscope was partly covered, and the electric spark between iron points passed in front of the slit. We had thus on the plate the photograph of the flash as well as of the spark. Fourteen more lines in the indigo and violet were thus identified with iron lines; and on extending the photographs into the ultra-violet, and substituting quartz lenses and prisms for the glass ones hitherto used, a much larger number of lines were identified. There could be no doubt, then, that we had iron vapour in the flash. We supposed that it must be derived from dust of oxide shaken by the explosion off the sides of the tube, and we had the tube bored out clean and bright like a gun-barrel. This made no diminution in the brightness or number of the lines; and we came to the conclusion that the explosion detached particles of iron from the tube, and converted them into vapour. This was confirmed by finding that, however carefully the tube had been cleaned, the glass ends always became clouded with a rusty deposit after ten or twelve flashes. Altogether 68 lines of iron have been identified in the flash, of which about 40 lie in the ultra-violet between H and O. Only one iron line above O has been definitely identified, and that in only a few photographs. It is T.

As iron gave so many lines in the flash it was reasonable to suppose that more volatile metals would give their lines too. Linings of thin sheet copper, lead, cadmium, zinc, aluminium, and tin were successively put into the tube, and their effects on the flash observed. Copper gave one strong line in the green (wave-length 5104.9), but no other line in the visible part

of the spectrum. In the ultra-violet two strong lines between Q and R came out in the photographs, frequently as reversed lines. Some of the photographs shewed also something of the shaded bands in the blue which are ascribed to the oxide of copper. The green line of copper had been observed in the flash before the copper lining was put into the tube; and we concluded that the copper was derived from the brass with which the small lateral tubes were fastened into the large tube, or that the iron of the tube contained a little copper. When the leaden lining was used, only one visible line of lead was developed, and that was the strong violet line, but two ultra-violet lines between M and N were strongly depicted on the photographic plates. The violet line of lead had also been observed in many of the photographs taken before the leaden lining was introduced. This we ascribed to the leaden washers used to make the glass or quartz plates airtight. The line was greatly increased in strength by the leaden lining. The zinc lining gave no visible line at all, notwithstanding the easy volatility of the metal; and in the ultra-violet it gave only a very doubtful impression of one of the lines near P. The cadmium, aluminium, and tin linings gave no lines at all. Zinc dust put into the tube gave no zinc lines, merely increased the continuous spectrum, and speedily rendered the quartz end opaque.

A clean wire of magnesium put into the tube gave the *b* group of lines, but no other line. No trace of the blue line, so conspicuous in the flame of burning magnesium, nor of the triplets near L and S, nor of the very strong line, the strongest of all in the arc, at wave-length 2852. b_1 and b_2 were well seen; but as b_4 is an iron line, as well as a magnesium line, and the iron line was visible in the flash before the magnesium wire was introduced, we cannot be sure whether the magnesium line, as well as the iron line, was present in the flash. Magnesia did not develop any line at all; merely augmented the continuous spectrum.

Compounds of sodium, such as the carbonate and chloride, introduced in powder gave the ultra-violet line between P and Q strongly, frequently reversed; but no other line except of course D. Potassium compounds developed, often reversed, the pair of violet lines, and also the ultra-violet pair near O, but no others.

A strip of silver developed two ultra-violet lines, one on either side of P; but we could not detect in the flash the well-known green lines of that metal. When powder of silver oxalate was introduced, the yellowish-green line (wave-length 5464) was seen at the first explosion but not afterwards. As silver oxalate is itself an explosive compound, decomposing with an evolution of heat, it is reasonable to ascribe the appearance of this line at the first explosion to the extra temperature so engendered.

Strips of copper, electroplated with nickel, brought out almost all the strong nickel lines in the ultra-violet between K and Q; 25 were

photographed. When nickel oxalate was put in so as to give a powder of metallic nickel after the first explosion, the same lines were developed, and three additional lines in the ultra-violet. Only one line was seen in the visible part of the spectrum, and that was the yellowish-green line (wave-length 5476).

Copper wires electroplated with cobalt gave in the flash 22 lines in the violet and ultra-violet, between G and P; no lines beyond those limits. Cobalt oxalate gave no more.

No other metal gave anything like so many lines as iron, nickel, and cobalt; and it is remarkable that almost all the lines of these metals developed in the flash lie in the same region between G and P.

We expected that manganese would have given several lines in the flash; but it was not so. Neither metallic manganese, nor any of several compounds which we tried, gave us any lines of that metal except the violet triplet, and this was generally given by the iron tube alone, and was merely stronger for the manganese put in. The green channellings characteristic of manganese, and ascribed to the oxide, were, however, well seen when metallic manganese was used.

Chromium, introduced as bichromate of ammonia, which of course became chromium oxide at the first flash, gave three triplets in the green, the indigo, and the ultra-violet near N respectively, but no other lines.

Bismuth, antimony, and arsenic gave no lines, nor did mercury spread over a sheet of copper lining the tube. Several metals were tried as amalgams spread over such a piece of copper, but with no fresh results, except in the case of thallium, which gave the green line strongly, the strong line between L and M, and two lines between N and O.

On the whole it does not appear that the form in which the metal is introduced into the tube makes much difference. The merest traces of those which gave lines were sufficient. Generally when a metal had been put into the tube, its lines continued to shew after the strip or lining had been removed. Thus, after the nickel strips had been taken out, and the tube cleaned out as completely as it could be mechanically, the nickel lines still came out in the flash, and the same was the case with other metals.

The strongest part of the water-spectrum, from *s* to near R, generally impressed itself more or less on the photographic plate; but, with the exception of T, which was only developed once or twice, no lines made their appearance in the region more refrangible than *s*.

Thus far the experiments had been made with the gases at the atmospheric pressure, or nearly so, before ignition. The proportions of hydrogen and oxygen were nearly two to one; but an excess of either gas to the extent of one-fifth did not sensibly affect the results.

Other explosive mixtures were tried. Carbonic oxide with oxygen, and marsh-gas with oxygen, developed in general the same lines as the hydrogen mixture, but gave a much brighter continuous spectrum. Sulphuretted hydrogen, arseniuretted hydrogen, and antimoniuiretted hydrogen, exploded with oxygen, also gave very bright continuous spectra, but no lines attributable to sulphur, arsenic, or antimony.

We have also tried explosions at higher pressures; mixtures of hydrogen, carbonic oxide, and marsh-gas respectively, with oxygen, were compressed into the tube by a condensing syringe until the pressure reached two and a half atmospheres, and in some cases three and a half atmospheres. The general effect of increasing the pressure was to strengthen very much the continuous spectrum, and also to intensify the bright lines, so that photographs could be taken with a smaller number of explosions. The lines previously observed to be reversed were more strongly reversed, but no new lines which we can attribute to the metals employed were noticed. No iron line more refrangible than T shewed itself in the photographs. But a banded spectrum, of which traces had been noticed in the flash of the gases at lower pressure, came out decidedly. This spectrum occupies the region between P and R; it is not a regularly channelled spectrum, though probably under higher dispersion it would resolve itself into groups of lines like the water-spectrum. In fact it seems to us most probable that it is a development of the water-spectrum, dependent on the pressure.

It seems very remarkable that metals so little volatile as iron, nickel, and cobalt should develop so many lines* in the flash, while more volatile metals shew few or no lines. We do not know that any lines attributed to the metals, as distinct from their compounds, which have been observed in the gas-flame cannot be seen also in the flash of the exploding gases, unless they be the blue lines of zinc which Lecoq de Boisbaudran has seen faintly in the gas-flame when zinc chloride was introduced. These are, however, so faint in the flame, that they might easily escape notice in the much stronger continuous spectrum of the flash. But iron, nickel, and cobalt shew no lines of those metals in a gas-flame. Mitscherlich (*Ann. d. Phys. u. Chem.* Bd. 121, St. 3, p. 469), by mixing vapour of ferric chloride with the hydrogen burnt in an oxy-hydrogen jet, obtained a number of the lines of iron. These form three groups—one below D, one near E, and one near G. The last two groups have a general correspondence with the lines developed in the explosions in the visible part of the spectrum; but exact identification is not possible with his figure. Of other metals he seems also to have found the same lines in the oxy-hydrogen jet which we have seen in the explosions, but with additional lines in several cases. Thus he found three zinc and as many cadmium lines, two of mercury, four of copper, and so on.

* For detailed list of these lines see *supra*, pp. 299–301.

Gouy (*C. R.*, Vol. 84, 1877, p. 233) has observed in the inner green cone of a modified Bunsen burner fed with gas mixed with spray of iron-salts, four green lines of iron which we did not find in the flash. He saw two of the blue lines, but not the other lines which we have noticed. In like manner with cobalt, he observed two feeble blue rays which we did not see in the explosions; also one zinc, one cadmium, and one silver line which we did not see; and he did not notice the green copper line which we always have seen in the explosions. In other cases he has noticed the same lines that we have noticed.

Comparing the spectrum of the explosions with that of iron wire burnt in a jet of coal-gas fed with oxygen, they may be called identical. We find in them generally the same lines and the same relative strengths of the lines. For instance, in the explosion-spectrum the strength of the groups of lines on either side of M and the line at wave-length 3859.2 is decidedly greater as compared with the other lines than it is in the arc-spectrum of iron. It is the same in that of iron burnt as above-mentioned. T, however, comes out more strongly in the last-mentioned spectrum than in the explosions.

German-silver wire burnt in the coal-gas and oxygen jet gave the same nickel and copper lines as were developed in the explosions. Silver wire gave in the same jet the two silver lines near P, but no channelled spectrum. Spray of cobalt chloride gave also the same lines as in the explosions, with a few additional; while spray of manganese chloride gave the strong manganese triplet at wave-length about 2800, more refrangible than anything observed in the explosions, besides the usual violet triplet.

On the whole the spectra produced by the jet of coal-gas and oxygen are very similar to those of the explosions as far as the metallic lines go; they exhibit a few more lines, or it may be these are more easily observed.

Of the green and blue lines of iron seen by us in explosions nine are registered by Watts as occurring in the flame of a Bessemer converter; or at least the lines he gives are so near that we cannot doubt their identity.

When we come to make a comparison with the spectrum of the spark-discharge from a solution of ferric chloride, the differences become more marked. Not only are there many more lines in the spark-spectrum, but the relative intensities of those lines which are common to both spark and explosion are very different, and two of the iron lines seen in the explosions appear to be absent from the spark. The differences between the spectrum of the spark taken from a liquid electrode and that given by solid electrodes has usually been attributed to the lower temperature of the former; but the absence from the former spectrum of the line at wave-length 4132, and the feebleness of the line at wave-length 4143, both strong lines in the arc and

in the explosions, as well as in the spark between solid electrodes, seem to indicate that the differences of spark-spectra are not simply due to differences of temperature. In fact we know so little about the mechanism, so to speak, of the changes of electric energy into heat, and of heat into radiation, that there is no good reason for assuming that the energy which takes the form of radiation in the electric discharge through a gas must first take the form of the motion of translation of the particles on which temperature depends. The gas may, for a short time, be intensely luminous at a very low temperature; and if the impulses which give rise to the vibratory movements of the particles be of different characters, the characters of the vibrations also may differ within certain limits.

Leaving, however, the realms of speculation, we may mention that we have before observed the spectrum of iron at a temperature intermediate between that of the oxy-hydrogen jet and that of the electric arc.

Some time since (*supra*, pp. 232 and 250) we described the spectrum proceeding from the interior of a carbon tube strongly heated by the electric arc playing on the outside. This spectrum approaches more nearly to that of the arc inasmuch as it shews all, or almost all, the iron lines given by the arc between F and O, and the aluminium pair between H and K; but it resembles the explosion-spectrum in the relative strength of some of the iron lines, and in the absence of almost all iron lines between O and T. The iron lines seen reversed against the hot walls of the carbon tube correspond with the strongest of the explosion lines; the strong lines near M and a little below L in the explosions being those most strongly reversed in the photographs of the carbon tube. The greater completeness and extent of the iron spectrum, as well as the presence of the aluminium lines, which are entirely wanting in the explosion-spectrum, indicate that the temperature of the tube was higher than that of the explosion. That iron, nickel, and cobalt are volatile in some degree at the temperature of the explosion appears to be proved, and makes the appearance of iron lines at the very apices of solar prominences, as observed by Young, less astounding than it seemed to be at first sight. The ascending current of gas making the prominence may very well carry iron vapour with it; or we may not unreasonably suppose that there is meteoric dust containing iron everywhere in the outer atmosphere of the sun, which becomes volatilized, and emits the radiation observed, when it is heated up by the hot current of the prominence. What the temperature of such a current may be we cannot well gauge, but it is high enough to give the hydrogen-spectrum, of which no trace has been observed in the flash of the explosions or in the oxy-hydrogen jet. The temperature of the explosions we know with tolerable accuracy, at least when the gases are at atmospheric pressure to begin with. Bunsen (*Phil. Mag.*, Vol. xxxiv, 1867, p. 494) found the pressure of the

explosion was for hydrogen and oxygen 9·6 atmospheres, and for carbonic oxide and oxygen 10·3 atmospheres, and he calculated the corresponding temperatures to be 2844° and 3033°. Recently published observations by Berthelot and Vieille (*Comptes Rendus*, 1884, p. 548) put the pressure of explosion of oxygen and hydrogen at 9·8 atmospheres and of carbonic oxide and oxygen at 10·1, and the corresponding temperatures 3240° and 3334°. The pressures determined by the two observers agree closely, and the calculated temperatures are not very discordant. On the whole, we cannot be wrong in assuming the temperature of the exploding gases to be about 3000°; and we see that at this degree such metals as iron, nickel, and cobalt are vaporous and emit many characteristic rays, and that by far the greatest part of these rays lie between narrow limits of refrangibility G and P. Even for other metals there is a predominance of rays in the same part of the spectrum. The lines of lead, potassium, and manganese, three out of four lines of thallium, and two-thirds of those of chromium, observed in the explosions, fall within the same region. It must not be inferred that these facts indicate the limit of the rate of oscillation which can be set up in consequence of an elevation of temperature to 3000°, because we know that the spectrum of the lime-light extends much further. But it might be possible to establish a sort of spectroscopic scale of temperatures if the lines which are successively developed as the temperature rises were carefully noted. Thus the appearance of the iron line T seems to synchronize with temperature of about 3000°. The lithium blue line is invisible in the flame of an ordinary Bunsen burner, but is just visible at the temperature of the inner green cone formed by reducing the proportion of gas to air in such a burner, while in the exploding gas the green line too is seen. It seems to need a temperature above 3000° to get the aluminium lines at H. Probably no line is ever abruptly brought out at a particular temperature—it will always be gradually developed as the temperature rises; yet the development may be rapid enough to give an indication which may be useful in default of means of more exact measurement. In former papers treating of spectroscopic problems (*supra*, pp. 77 and 241) we have more than once adverted to the necessity of the study of the spectra both of flames and of the electric discharge under modified conditions of pressure. The projected experiments on the arc in lime-crucibles have not yet been carried out; but the present is a first instalment of a study of flame-spectra under such conditions.

NOTE ON A NEW FORM OF DIRECT VISION SPECTROSCOPE

[*Proceedings of the Royal Society*, Vol. XLI. (1886), pp. 449 sqq.]

DIRECT vision spectroscopes are very useful in the observation of shifting objects, such as auroræ and other meteors. They are generally in request for telescopic work, and also in all cases where rapidity of observation is of consequence. Ordinary direct vision spectroscopes with compound prisms have the disadvantage that the dispersion of the red end of the spectrum is small; less in proportion to that of the blue end than in spectroscopes with simple prisms. Also no measurements of lines can be made with them, except by means of a scale fixed in the field of view, which it is often difficult to see for want of illumination.

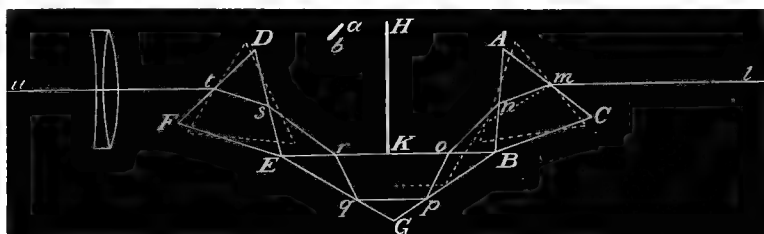
Some time since (*supra*, p. 39) we brought under the notice of the Society a direct vision spectroscope on Thollon's plan, which had not the faults of the instruments with compound prisms. It gave a dispersion equal to that of two prisms of 60° , and excellent definition, but the number of reflecting and refracting surfaces which had to be truly wrought was rather large, and the movement of the prisms by a screw made measurements with it slow.

Since then we have tried a spectroscope with one of the Astronomer Royal's half prisms, but we found it impossible to get good definition with the half prism for more than a small part of the visible spectrum; and in consequence faint bands near either end of the spectrum were quite invisible with this instrument.

The arrangement we have now to describe was intended to obviate the defects of the others.

It has three prisms symmetrically arranged, the middle one serving both for refraction and reflexion. The course of a ray through the prisms is indicated in the annexed diagram. A ray lm in the line of the axis of the collimator meets the first prism ABC in m , is refracted at m and n , meets the second prism EGB at o , and is then refracted, undergoes two internal reflexions at p and q , and is refracted out at r ; it is then refracted through the third prism DEF at s and t , and emerges in the direction tu ,

which is a prolongation of its original direction lm and coincides with the axis of the observing telescope. The prism EGB is fixed, the other two prisms are movable about axes parallel to their edges passing through the points m and t . They are rotated simultaneously in opposite directions by a pair of linked levers, of which one carries a graduated arc of $9\frac{1}{2}$ inches radius, by which the angle of rotation can be determined. Those rays which suffer no deviation in passing through the train, must all follow a course through the fixed prism parallel to $opqr$, whatever their refrangibility; but the angle of incidence at o will be different for the different values of the refractive index. By turning the two movable prisms into the positions shewn by dotted lines the angle of incidence at o will be diminished, and a less refrangible ray will follow the course of no deviation. If then the first position of the prisms ABC , DFE be that for which an extreme violet ray incident in the line lm suffers no deviation, all the less refrangible rays incident in the same direction may be successively brought to suffer no deviation by turning the prisms towards the position shewn by the dotted



line. The angles of the prisms have, of course, to be adjusted so that the extreme violet ray may suffer no deviation. A simple calculation suffices for this when the refractive indices of the glass employed are known. We have had the fixed prism constructed with the acute angles about $33\frac{1}{4}^\circ$, and the movable prisms with angles about 62° . With these angles, when the movable prisms are so placed that the angles of incidence at m and of emergence at n are equal (the position of minimum deviation), the ray which suffers no deviation is one somewhat more refrangible than K of the solar spectrum. When then the prisms are turned, less refrangible rays are successively brought into the field of view, but no ray much more refrangible than K can be brought into the field. By increasing the acute angles of the fixed prism, or by diminishing the angles of the movable prisms, a longer range can be given to the instrument, but at the expense of some dispersion.

To prevent light passing directly from the collimator to the observing telescope, a stop HK is placed midway between the movable prisms.

It will be observed that the fixed prism serves both as a reflector and refractor, the dispersion produced by it being the same as that of a simple

refracting prism of 46° (or $180^\circ - 4EBG$) in the position of minimum deviation. The dispersion for the extreme violet is therefore that of two prisms of 62° and one of 46° in the position of minimum deviation. For less refrangible rays the position of the movable prisms is not that of minimum deviation and the dispersion is proportionally increased, so as to help, in a small degree, to correct the inequality of dispersion of the two ends of the spectrum. At the same time the symmetry of the arrangement is maintained for all rays when in mid-field, and sharp definition is secured for all parts of the spectrum. This is a most important character. We find that with our instrument A and H of the solar spectrum are equally well seen, and so are the red and violet lines of the flame spectrum of potassium.

For greater convenience in manipulation, and at the same time to ensure a large angular aperture, our instrument has a short collimator and telescope. The magnification of the image is in consequence but small, but nevertheless it is easy to see the nickel line between the two D lines in the solar spectrum, and the large angular aperture makes it easier to see faint spectra from large objects, as well as to catch the light of a moving object. With an eye-piece of low power it serves well for the observation of absorption spectra.

Measurements are made with it by bringing the line of which the position is to be measured to a fixed pointer in the middle of the field of view. The whole angle through which the prisms have to be moved in passing from A to H is $10^\circ 15'$, and as it is easy to read quarter minutes with the vernier, considerable accuracy of measurement may be attained. It must be observed, however, that the change of angle is not proportional to the change of refrangibility of the rays brought to mid-field, because a larger proportional rotation is required at the violet end, when the prisms are near the position of minimum deviation, than at the red end. Still there is a rotation of $33' 30''$ in passing from A to B. .

The prisms are enclosed in a box, and though this is an advantage in viewing faint spectra, it would sometimes be difficult to see the pointer without some means of illuminating either the pointer or the field. We effect the latter object by a slit in the side of the box, and a small white paper reflector, *ab* in the figure, which throws light from the opening in the box on to the side of the object glass, clear of the prism. The slit in the box may be closed with a shutter or with glasses of different colours.

Lastly, the instrument can be used either with or without a stand. Without the stand it is light enough to be held in the hand and directed to the sky or to a moving object.

It has been constructed for us by Mr Hilger with his usual skill.

ON THE SPECTRUM OF THE OXY-HYDROGEN FLAME

[*Proceedings of the Royal Society*, Vol. XLIII. (1888), p. 347]

(*Abstract.*)

IN a former communication the authors described simultaneously with Dr Huggins the strongest portion of the spectrum of water, subsequently they described a second less strong but more refrangible section of the same spectrum. M. Deslandres has noticed a third still more refrangible section. The authors now find that the spectrum extends, with diminishing intensity, into the visible region on the one hand, and far into the ultra-violet on the other. These faint parts of the spectrum they have photographed, using the dispersion of a single calcite prism and a lengthened exposure; and in the present communication they give a map of the whole extent observed, and a list of wave-lengths of upwards of 780 lines.

The spectrum exhibits the appearance of a series of rhythmical groups more or less overlapping one another, and the arrangement of the lines in these groups is shewn to follow, in many cases, the law that the distances between the lines, as measured in wave-lengths, are in an arithmetic progression. M. Deslandres had previously announced that the succession of lines in A, B, and α follow this law when their distances are measured in reciprocals of wave-lengths, and he has stated that the groups A, B, and α have counterparts in the spectrum of water. The authors find a striking resemblance between those groups and certain parts of the water spectrum, but no exact correspondence.

Dr Grünwald, of Prague, predicted on theoretical grounds that certain lines would appear in the spectrum of water, and the authors have found a considerable number of lines which tally closely with Dr Grünwald's predictions, some of them, in the extremities of the spectrum, being the strongest lines observed in those regions.

ON THE SPECTRUM OF THE OXY-HYDROGEN FLAME

[*Philosophical Transactions of the Royal Society*,
Vol. 179 (1888), pp. 27 sqq.]

IN 1880 we described, simultaneously with Dr Huggins, a series of lines forming the strongest part of the spectrum of water, and again, in 1882, a second, less strong and more refrangible, series, forming a second section of the same spectrum. Subsequently, M. Deslandres discovered a third still weaker and more refrangible series, beginning at a wave-length 2610·3. We find, however, that the spectrum does not end there, but extends both on the more refrangible and on the less refrangible sides to a considerable distance. By employing a large spectroscope with a single calcite prism and a long exposure we have obtained photographs of the spectrum of the oxy-hydrogen flame, shewing closely set lines from wave-length 2268 to 4100, with traces of lines beyond those limits. The whole spectrum appears to consist of a succession of rhythmical series of lines, the lines of each rhythmical series being stronger and more closely set at the more refrangible end of the series and becoming weaker and wider apart towards the less refrangible end. The strongest of these series are those first described, those on either side of them becoming fainter as they are more remote, until the highest series gave us a measurable photograph only after an exposure of five hours. In most cases two series begin near together and overlap one another, producing a complication which cannot easily be unravelled, and the overlapping appears in some cases to extend to more than two series.

M. Deslandres states (*Comptes Rendus*, Vol. 100, p. 854) that the first band of the water spectrum (*i.e.* the group beginning at a wave-length about 3063) includes a series of rays which reproduce, line for line, at the same distances and with the same relative intensities, the band A of the solar spectrum; and that the second band (*i.e.* the group beginning at a wave-length about 2811) includes a series corresponding to B, and that in the third α may be found to be reproduced. He does not state at what wave-lengths in these bands we are to look for the more refrangible edges of A, B,

and α respectively; and we have not been able to make out such an exact correspondence between the lines of the water spectrum and those of A, B, and α as M. Deslandres' words seem to imply. Nevertheless, the similarity of the grouping is very remarkable, as may be seen from the accompanying map, on which are given the lines of A, on a scale slightly reduced from Professor Piazzzi Smyth's solar spectrum, side by side with the lines of the water spectrum. The correspondence of B and of α to certain lines of the higher groups is less striking. We have no doubt that the peculiar arrangement of the lines, commencing at the more refrangible end with some closely set lines and continued in a series of doublets, is in all these cases the result of a general law.

The tables of wave-lengths which follow were obtained by measuring the distances of the lines from those of iron photographed on the same plate through a part of the slit. The whole of the lines previously measured have been re-measured, and the numbers assigned as their wave-lengths corrected by reference to more recent measurements of the iron lines. The scale is, however, that of Ångström. On account of the faintness of the rays at the two extremities of the spectrum a wide slit had to be employed, as well as a lengthened exposure in photographing them, consequently the photographed lines are broad and somewhat ill-defined, and groups of closely set lines could not be resolved. The wave-lengths in the first and last tables are therefore liable to greater errors than those in the intervening tables. Moreover, in these parts, the spectrum is so weak that the strongest line is less intense than the weakest lines of the region about λ 3100, and it has been found necessary to adopt a different scale of intensities for different sections.

It is, perhaps, worth remarking that there is a broad diffuse line, the strongest of the lines in that region, coincident with K of the solar spectrum. There is no line coincident with H.

TABLES of wave-lengths, and inverse wave-lengths, of the lines in the spectrum of the oxy-hydrogen flame. The numbers prefixed represent the intensities 1 to 6, No. 1 being the most intense. Diffuse lines are noted with a *d*.

I.

Intensity	λ	$\frac{1}{\lambda}$	Intensity	λ	$\frac{1}{\lambda}$	Intensity	λ	$\frac{1}{\lambda}$
6	2268.0	44,092	6	2374.9	42,107	6	2412.1	41,459
6	2272.2	44,010	6	2375.5	42,096	6 <i>d</i>	2412.6	41,450
6	2283.6	43,791	6	2376.6	42,077	6	2414.3	41,420
6	2297.0	43,535	6	2378.6	42,042	6	2414.8	41,411
6	2300.8	43,463	6	2379.6	42,024	5	2416.2	41,387
6	2307.5	43,337	6	2381.9	41,983	6	2418.0	41,356
6	2310.1	43,288	6	2383.0	41,964	6	2419.8	41,326
6	2316.2	43,174	5	2384.3	41,941	6	2421.6	41,295
5	2323.8	43,033	4	2385.7	41,916	6	2422.4	41,281
6 <i>d</i>	2331.1	42,898	5	2387.0	41,894	4	2425.7	41,225
6 <i>d</i>	2332.2	42,878	6	2390.6	41,831	6	2427.0	41,203
5	2337.5	42,781	6	2391.6	41,813	5	2428.1	41,184
6	2342.1	42,697	6	2393.5	41,780	5	2429.7	41,157
6	2345.6	42,633	6	2394.8	41,757	6 <i>d</i>	2431.2	41,132
6	2347.5	42,599	6	2396.3	41,731	6 <i>d</i>	2431.8	41,122
6	2351.6	42,524	6	2398.0	41,702	6	2433.3	41,096
6	2354.1	42,479	6	2398.6	41,691	6 <i>d</i>	2433.9	41,086
5	2355.5	42,454	5	2399.4	41,677	6	2435.9	41,053
6	2356.6	42,434	5	2402.4	41,625	6	2437.2	41,031
6	2357.7	42,414	6	2403.2	41,611	5	2438.7	41,005
6	2360.6	42,362	6	2404.2	41,595	5	2440.3	40,979
6	2365.1	42,282	6	2405.4	41,574	6	2441.6	40,957
6	2366.1	42,264	6	2406.6	41,553	6	2443.2	40,930
6	2368.6	42,219	6	2407.6	41,536	6	2445.4	40,893
6	2371.2	42,173	5	2409.0	41,511	6	2446.5	40,875
6	2372.8	42,144	6	2410.1	41,492	6	2448.4	40,843
6	2373.6	42,130						

II.

The average intensities of the lines in this section are greater than those of the lines in the preceding section, so that a line marked No. 6 in the following table is generally quite as intense as one marked No. 4 in the preceding table.

Intensity	λ	$\frac{1}{\lambda}$	Intensity	λ	$\frac{1}{\lambda}$	Intensity	λ	$\frac{1}{\lambda}$
4	2449.3	40,828	5	2498.0	40,032	6	2545.6	39,283
5	2450.9	40,801	6	2499.8	40,003	4	2547.7	39,251
6	2452.2	40,780	5	2501.4	39,978	4d	2550.3	39,211
6	2453.3	40,761	5	2503.1	39,950	3	2553.4	39,163
5	2454.7	40,738	6	2503.7	39,941	4	2556.4	39,118
4	2456.0	40,717	6	2504.0	39,936	3	2559.6	39,069
5	2457.7	40,688	6	2504.4	39,930	5	2562.6	39,023
6	2459.2	40,664	6	2505.2	39,917	6	2565.6	38,977
6	2460.0	40,650	6	2505.6	39,911	5	2567.0	38,956
6	2461.7	40,622	6	2506.8	39,892	5	2569.1	38,924
4d	2462.8	40,604	6	2508.1	39,871	6	2570.4	38,904
6	2464.5	40,576	6	2509.1	39,855	6	2572.9	38,867
6	2465.9	40,553	6	2509.8	39,844	6	2573.4	38,859
6	2467.1	40,533	6	2510.5	39,833	6	2574.5	38,842
5	2469.6	40,492	6	2511.1	39,823	6	2576.7	38,809
4	2471.9	40,455	6	2513.1	39,791	6	2578.3	38,785
6	2474.5	40,412	6	2515.1	39,760	6	2580.9	38,746
6	2477.6	40,362	5	2517.5	39,722	6	2582.1	38,728
6	2479.3	40,334	5	2519.8	39,686	6	2582.8	38,718
6	2480.7	40,311	5	2521.7	39,656	5	2584.4	38,694
5	2482.6	40,280	5	2524.2	39,617	6	2587.1	38,653
6	2483.7	40,263	6	2529.2	39,538	5	2589.1	38,623
6	2484.9	40,243	4	2530.2	39,523	6	2591.3	38,591
6	2485.8	40,229	6	2531.4	39,504	6	2592.8	38,568
5	2487.2	40,206	5	2534.1	39,462	6	2594.6	38,542
5	2489.3	40,172	3	2536.6	39,423	6	2596.4	38,515
4	2491.1	40,143	5	2537.7	39,406	6	2598.6	38,482
6	2492.3	40,124	6	2538.9	39,387	6	2600.9	38,448
6	2493.8	40,099	6	2540.2	39,367	6	2603.2	38,414
6	2495.6	40,071	6	2542.7	39,328	6	2605.2	38,385
5d	2496.3	40,059						

III.

The average intensities of the lines in this section are a good deal greater than that of the lines in the preceding section, so that intensity No. 6 in this table would include lines of intensity No. 4 in the preceding section.

Intensity	λ	$\frac{1}{\lambda}$	Intensity	λ	$\frac{1}{\lambda}$	Intensity	λ	$\frac{1}{\lambda}$
3	2608.4	38,338	4	2673.2	37,409	6	2734.3	36,572
6	2608.9	38,331	6	2675.8	37,373	5	2735.5	36,557
6	2609.7	38,319	3	2677.3	37,352	4	2737.8	36,526
5	2611.0	38,300	6	2678.2	37,339	4	2740.2	36,494
6	2612.6	38,277	6	2679.0	37,327	6	2742.7	36,460
4d	2613.5	38,264	4	2680.9	37,302	4	2745.9	36,418
4	2614.6	38,247	6	2681.8	37,288	4	2748.3	36,387
6	2615.6	38,232	Band	{ 2683.0	37,272	5	2751.0	36,351
5	2616.5	38,219		{ 2683.7	37,263	5	2753.1	36,323
6	2617.0	38,212	6	2684.8	37,247	6	2754.7	36,302
5	2617.7	38,201	5	2685.5	37,238	4	2757.0	36,271
6	2618.1	38,196	6	2686.5	37,224	6	2759.0	36,246
4	2618.9	38,184	6	2687.2	37,213	4d	2759.8	36,235
5	2620.6	38,159	5	2687.7	37,207	4	2761.4	36,214
5	2621.4	38,148	4	2688.9	37,191	6	2762.6	36,198
6	2622.2	38,136	5	2690.6	37,167	4	2764.1	36,178
6	2622.8	38,128	5	2691.7	37,152	5	2766.3	36,150
6	2623.3	38,120	6	2692.5	37,140	6	2767.3	36,137
3d	2624.3	38,105	6	2693.2	37,131	6	2768.2	36,125
5	2625.9	38,083	5	2693.8	37,123	6	2769.1	36,113
6	2627.2	38,063	5	2695.4	37,101	6	2770.0	36,101
5	2627.7	38,057	6	2696.1	37,091	6	2770.9	36,090
5	2628.3	38,047	6d	2697.8	37,067	6	2772.3	36,071
2d	2631.3	38,004	4	2698.8	37,054	6	2773.8	36,052
5	2632.4	37,988	6	2699.7	37,041	5	2774.9	36,037
6	2633.4	37,974	3	2701.6	37,016	5	2776.1	36,022
5	2634.8	37,954	6	2704.3	36,979	6	2777.4	36,005
4	2635.7	37,941	5	2705.2	36,966	6	2778.6	35,989
6	2636.9	37,924	5	2706.2	36,952	5	2779.2	35,982
4	2638.5	37,900	6	2707.2	36,939	6	2780.7	35,962
3	2640.5	37,872	4	2709.6	36,907	4	2783.2	35,930
6	2642.2	37,847	6	2710.6	36,893	6	2784.8	35,909
5	2643.1	37,834	4	2711.6	36,879	4	2786.5	35,887
6	2644.2	37,819	6	2713.6	36,851	6	2787.7	35,872
3	2645.7	37,797	4	2714.5	36,839	6	2788.3	35,864
3	2648.2	37,762	5	2715.8	36,822	6	2789.1	35,854
6	2650.7	37,726	4	2717.2	36,803	6	2789.8	35,845
3	2651.3	37,717	6	2718.2	36,789	5	2790.5	35,836
6	2652.6	37,699	4	2719.8	36,767	6	2791.7	35,820
5	2653.7	37,684	5	2721.6	36,743	5	2793.8	35,794
6	2654.3	37,675	4	2723.5	36,717	6	2795.7	35,769
2	2657.4	37,631	5	2724.8	36,701	5	2796.9	35,754
4	2659.7	37,698	5	2726.1	36,682	6	2797.6	35,745
5	2660.9	37,581	5	2728.2	36,655	3	2799.8	35,717
3	2663.9	37,539	6	2729.9	36,631	5	2802.9	35,677
5	2666.0	37,501	4	2730.6	36,623	6	2804.2	35,661
5	2668.1	37,480	4	2732.1	36,602	6	2805.4	35,646
3	2671.1	37,438	5	2733.0	36,590	5	2806.8	35,628

IV.

The lines of this section are generally much more intense than those of the preceding section, so that intensity No. 6 of this section may include lines which would be marked as of intensity 4, according to the scale employed in the preceding section.

Intensity	λ	$\frac{1}{\lambda}$	Intensity	λ	$\frac{1}{\lambda}$	Intensity	λ	$\frac{1}{\lambda}$
3	2811.2	35,572	3	2857.6	34,994	5	2918.2	34,268
6	2811.3	35,571	3	2859.4	34,972	2d	2918.5	34,264
6	2811.7	35,566	3	2860.3	34,961	4	2919.8	34,249
6	2812.1	35,561	3	2861.7	34,956	4	2921.5	34,229
6	2812.4	35,557	3	2863.3	34,925	5	2923.8	34,202
4d	2813.5	35,543	6	2865.5	34,898	4	2924.4	34,195
5	2814.9	35,525	3	2866.0	34,892	4	2924.8	34,190
4	2815.6	35,516	3	2868.3	34,864	4	2926.3	34,173
4	2816.1	35,510	3	2869.5	34,849	5	2927.1	34,164
3	2817.1	35,498	3	2871.5	34,825	5	2927.6	34,158
6	2818.2	35,484	3	2871.9	34,820	4	2929.9	34,131
4	2818.7	35,477	2d	2875.0	34,783	4	2931.0	34,118
6	2819.3	35,470	3d	2875.8	34,773	3d	2933.5	34,089
3	2820.1	35,460	2d	2878.3	34,743	5	2935.2	34,069
6	2820.7	35,452	5d	2880.3	34,719	6	2936.5	34,054
6	2821.2	35,446	6	2881.1	34,709	4	2937.2	34,046
3	2821.8	35,438	6	2881.8	34,701	3	2937.8	34,039
4	2822.3	35,432	4	2882.5	34,692	6	2938.5	34,031
6	2824.0	35,411	6	2884.2	34,672	4	2940.3	34,010
3	2824.8	35,401	3	2885.3	34,658	4	2940.6	34,007
4d	2825.2	35,396	6	2886.1	34,649	5	2944.2	33,965
3	2826.3	35,382	6	2886.3	34,646	3	2945.2	33,954
6d	2828.3	35,357	4	2887.5	34,632	6	2946.5	33,939
2	2828.7	35,352	6	2888.5	34,620	4d	2947.5	33,927
6	2829.2	35,346	6	2889.2	34,612	5	2948.5	33,916
4d	2829.8	35,338	3	2889.8	34,604	6	2950.1	33,897
4	2831.1	35,322	3	2890.2	34,600	6	2950.7	33,890
3	2831.7	35,314	5	2890.8	34,593	6	2951.2	33,885
4	2833.3	35,295	1	2892.9	34,567	6	2951.7	33,879
4	2834.0	35,286	5	2893.5	34,560	6	2952.5	33,870
3	2835.0	35,273	6	2894.2	34,552	6	2953.2	33,862
3	2835.8	35,263	4	2896.1	34,529	6d	2954.5	33,847
5	2836.7	35,252	6	2897.1	34,517	6	2955.5	33,835
1	2838.8	35,226	4	2897.6	34,511	6	2956.3	33,826
4	2840.1	35,210	4	2898.1	34,505	5	2957.1	33,817
6	2841.0	35,199	6	2898.8	34,497	6	2958.9	33,796
3	2842.2	35,184	4	2899.5	34,489	3	2960.0	33,784
3	2842.7	35,177	3	2900.2	34,480	6	2962.1	33,760
6?	2843.1	35,173	4	2900.9	34,472	5	2962.9	33,751
2	2844.4	35,157	6	2902.5	34,453	4	2965.5	33,721
6?	2845.4	35,144	1	2903.7	34,439	6	2966.5	33,710
3	2846.3	35,133	6	2906.0	34,412	6	2967.1	33,703
3	2847.4	35,120	5	2906.6	34,404	6	2968.0	33,693
3	2848.8	35,103	3	2907.3	34,396	6	2968.5	33,687
3	2849.5	35,094	3	2908.3	34,384	6	2970.0	33,670
3	2850.3	35,085	3	2909.4	34,371	5	2970.7	33,662
6	2850.7	35,079	3	2911.4	34,348	6	2971.1	33,658
2	2852.2	35,059	3	2912.9	34,330	6	2972.2	33,645
3	2853.9	35,040	5	2913.5	34,323	6	2973.9	33,626
3	2854.9	35,028	4	2915.7	34,297	3d	2975.1	33,612
3	2855.4	35,021	3	2916.3	34,290	3d	2977.8	33,582

Intensity	λ	$\frac{1}{\lambda}$	Intensity	λ	$\frac{1}{\lambda}$	Intensity	λ	$\frac{1}{\lambda}$
3d	2979.4	33,564	4	2997.8	33,358	6	3022.5	33,085
3d	2980.2	33,555	6	2998.7	33,348	6	3023.4	33,075
6	2982.2	33,532	4	3001.9	33,312	6	3025.2	33,056
6	2982.9	33,524	6	3005.0	33,278	6	3027.6	33,029
6d	2983.8	33,514	6	3005.6	33,271	6	3030.3	33,000
6	2985.7	33,493	6	3008.2	33,242	5	3033.1	32,970
6	2987.2	33,476	6	3008.8	33,236	5	3036.4	32,934
5	2988.5	33,462	6	3012.9	33,191	4	3039.9	32,896
6	2990.5	33,439	6	3016.6	33,150	4	3043.9	32,853
5	2991.7	33,426	6	3020.9	33,103	3	3048.3	32,805
6	2992.9	33,412	6	3021.4	33,097	3	3052.7	32,758
6	2994.8	33,391	6	3022.0	33,091	4	3057.4	32,708
4	2996.6	33,371						

V.

This section is the strongest part of the spectrum of the oxy-hydrogen flame. Lines marked as of intensity 4, on the scale of Table IV, would for the most part be marked as of intensity 6 on the scale of this table.

Intensity	λ	$\frac{1}{\lambda}$	Intensity	λ	$\frac{1}{\lambda}$	Intensity	λ	$\frac{1}{\lambda}$
2	3063.3	32,645	2d	3105.3	32,203	6	3148.0	31,766
4	3063.9	32,638	5	3106.0	32,196	3	3149.5	31,751
3	3064.6	32,631	3	3107.0	32,185	3	3150.6	31,740
4	3065.5	32,621	3	3108.8	32,167	4	3151.7	31,729
2d	3067.2	32,603	3	3109.7	32,157	6	3152.7	31,719
6d	3068.2	32,592	1	3111.5	32,139	2	3154.0	31,706
3	3070.0	32,573	3	3112.8	32,125	6	3156.4	31,682
2	3071.5	32,557	3	3114.3	32,110	6	3157.3	31,673
6	3072.6	32,546	4	3116.6	32,086	4	3158.0	31,666
5	3073.8	32,533	2	3117.4	32,078	5	3160.3	31,643
5	3074.4	32,527	4	3119.2	32,060	4	3161.5	31,631
5	3076.6	32,503	6	3121.3	32,038	6	3162.8	31,618
3	3077.9	32,490	2	3122.2	32,029	5d	3163.9	31,607
2	3079.3	32,475	3	3123.5	32,015	5	3166.0	31,586
2	3081.0	32,457	4	3124.5	32,005	2d	3169.1	31,555
3	3082.6	32,440	6	3126.0	31,990	6	3172.8	31,518
3	3084.6	32,419	6	3127.3	31,976	3	3174.0	31,506
5	3085.8	32,407	3	3127.8	31,971	6	3174.6	31,500
3	3086.7	32,397	2	3129.9	31,950	5	3177.2	31,474
1	3089.3	32,370	6	3130.8	31,941	6	3179.6	31,451
3	3089.8	32,365	5	3132.6	31,922	6	3181.0	31,437
2	3090.6	32,356	2	3133.7	31,911	4	3182.6	31,421
2d	3092.0	32,342	2	3136.3	31,885	3	3185.6	31,391
3	3094.2	32,319	6	3137.4	31,874	6	3187.6	31,372
3	3094.8	32,312	5	3138.7	31,860	5	3191.3	31,335
3	3095.8	32,302	6	3139.4	31,853	6	3191.9	31,329
3	3096.3	32,297	3	3140.3	31,844	4	3194.5	31,304
3	3098.3	32,276	6	3141.5	31,832	5	3198.7	31,263
2	3099.0	32,268	6	3142.5	31,822	5	3200.4	31,246
5	3100.6	32,252	3	3143.5	31,812	5	3201.9	31,231
2	3101.6	32,241	6	3145.1	31,795	5	3203.5	31,216
3	3102.7	32,230	2d	3146.9	31,777			

VI.

The lines of this section are weaker than those of the preceding section, so that in the scale of intensity of this table, No. 4 is not stronger than No. 6 of the preceding table.

Intensity	λ	$\frac{1}{\lambda}$	Intensity	λ	$\frac{1}{\lambda}$	Intensity	λ	$\frac{1}{\lambda}$
4d	3205.7	31,194	6	3293.0	30,367	5	3433.5	29,125
6	3208.1	31,171	2	3295.5	30,344	4	3435.4	29,109
6	3209.7	31,156	6	3298.7	30,315	4	3437.4	29,092
6	3212.0	31,133	6	3304.2	30,265	4	3439.7	29,072
3	3213.1	31,123	4d	3304.9	30,258	4	3442.3	29,050
6	3214.4	31,110	4	3307.5	30,234	4	3444.7	29,030
6	3215.9	31,095	6	3308.9	30,222	5	3447.6	29,006
4	3217.5	31,080	6	3310.5	30,207	6	3450.1	28,985
4	3220.0	31,056	5	3311.4	30,199	5	3451.0	28,977
4	3221.0	31,046	5	3314.8	30,168	6	3455.4	28,940
4	3222.8	31,029	4d	3318.0	30,139	5	3458.2	28,917
4	3224.6	31,012	6	3319.6	30,124	5	3459.5	28,906
4	3225.9	30,999	5	3321.8	30,104	5	3461.0	28,893
5	3229.3	30,966	6	3323.0	30,093	5	3462.6	28,880
6	3230.3	30,957	4	3325.4	30,072	5	3464.2	28,867
6	3230.9	30,951	5	3329.1	30,038	4	3465.9	28,853
4	3233.2	30,929	3d	3332.5	30,008	4	3467.7	28,838
4	3234.6	30,916	5	3335.9	29,977	5	3469.6	28,822
4	3237.9	30,884	6	3337.2	29,965	2	3471.9	28,803
4	3240.6	30,858	6	3344.2	29,903	5	3474.1	28,784
6	3242.3	30,842	6	3346.2	29,885	6	3475.5	28,773
2	3243.7	30,829	6	3347.3	29,875	4	3476.9	28,761
6	3248.4	30,784	6	3349.1	29,859	5	3479.1	28,743
6	3249.8	30,771	6	3352.3	29,830	6	3481.4	28,724
6	3250.5	30,765	6	3353.7	29,818	6	3482.9	28,712
4	3252.0	30,750	5	3355.9	29,798	4	3483.9	28,703
4	3253.2	30,739	5	3359.7	29,765	5	3486.2	28,685
4	3254.8	30,724	6	3362.2	29,742	6	3488.0	28,670
4	3256.4	30,709	6	3368.8	29,684	4	3489.5	28,657
6	3258.4	30,690	6	3370.1	29,673	6	3492.3	28,634
6	3260.7	30,668	6	3371.7	29,659	6	3493.3	28,626
6	3262.5	30,651	6	3373.2	29,645	6	3495.8	28,606
2	3263.6	30,641	6	3375.4	29,626	4	3497.2	28,594
2	3266.4	30,615	6	3377.6	29,607	4	3502.1	28,554
2	3268.5	30,595	6	3380.2	29,584	5	3507.6	28,510
6	3270.0	30,581	5	3383.3	29,557	6	3509.9	28,483
6	3271.4	30,568	6	3384.7	29,545	6	3511.6	28,477
4d	3273.7	30,546	5	3386.2	29,532	5	3513.3	28,463
4	3275.5	30,530	5	3390.3	29,496	6	3515.2	28,448
4	3276.3	30,522	5	3394.5	29,459	5	3517.2	28,432
4d	3278.3	30,504	5	3399.1	29,420	6	3519.0	28,417
6	3279.2	30,495	5	3404.2	29,375	6	3523.1	28,384
6	3281.2	30,477	5	3409.7	29,328	5	3524.1	28,376
6	3282.9	30,461	6	3412.8	29,301	6	3525.6	28,364
6	3284.3	30,448	5	3415.4	29,279	5	3527.3	28,350
6	3285.7	30,435	6	3418.3	29,254	5	3530.0	28,329
5	3286.9	30,424	6	3421.5	29,227	6	3531.8	28,314
5	3289.9	30,396	3d	3427.7	29,174	6	3533.6	28,300
5	3290.7	30,389	6	3428.5	29,167	6	3534.7	28,291
6	3291.8	30,379	3	3431.8	29,139	6	3536.7	28,275

Intensity	λ	$\frac{1}{\lambda}$	Intensity	λ	$\frac{1}{\lambda}$	Intensity	λ	$\frac{1}{\lambda}$
5	3538.2	28,263	5	3577.3	27,954	6	3631.6	27,536
5	3540.7	28,243	6	3578.7	27,943	4	3637.4	27,492
6	3542.4	28,229	5	3584.3	27,899	6	3645.3	27,433
6	3544.9	28,210	5	3592.0	27,840	4	3647.7	27,415
5	3547.7	28,187	5	3600.4	27,775	6	3651.1	27,389
4d	3552.3	28,151	6	3605.0	27,739	5	3653.1	27,374
5	3557.8	28,107	5	3609.0	27,709	4	3659.1	27,329
5	3559.3	28,095	4	3618.1	27,639	6	3668.2	27,261
5	3564.2	28,057	6	3625.3	27,584	4	3669.8	27,249
5	3570.4	28,008	4	3627.6	27,566			

VII.

The lines in this section are less intense than in the preceding section, and a line of intensity 4 on the scale of this table would be included in intensity 6 of the scale of the preceding table (VI).

Intensity	λ	$\frac{1}{\lambda}$	Intensity	λ	$\frac{1}{\lambda}$	Intensity	λ	$\frac{1}{\lambda}$
6	3673.3	27,223	4d	3779.0	26,462	6	3942.2	25,367
6	3674.6	27,214	6	3786.8	26,408	5	3947.1	25,335
6	3676.4	27,201	6	3789.6	26,388	5	3952.6	25,300
6	3678.2	27,187	6	3792.0	26,371	6	3960.1	25,252
6	3678.8	27,183	6	3794.0	26,357	6	3963.5	25,230
6	3681.5	27,163	4d	3799.7	26,318	6	3966.4	25,212
6	3681.9	27,160	5	3806.9	26,268	5	3973.8	25,165
6	3683.8	27,146	5	3811.1	26,239	5	3981.1	25,119
6	3684.7	27,139	5	3815.2	26,211	6	3990.3	25,061
6	3686.9	27,123	5	3821.7	26,166	5	3996.9	25,019
6	3688.0	27,115	5	3823.4	26,155	6	4006.7	24,958
6	3691.3	27,091	5	3828.4	26,121	6	4008.5	24,947
4d	3694.6	27,067	5	3832.5	26,093	5	4019.9	24,876
6	3700.1	27,026	6	3834.4	26,080	5	4026.0	24,839
6	3704.7	26,993	6	3841.1	26,034	5	4036.8	24,772
6	3707.0	26,976	5	3846.3	25,999	5	4049.7	24,693
5	3710.3	26,952	6	3850.8	25,969	6	4061.7	24,620
6	3716.5	26,907	5?	3852.0	25,961	6	4065.3	24,598
6	3719.7	26,884	6	3855.5	25,937	6	4073.1	24,551
5	3722.9	26,861	5	3859.1	25,913	6	4075.6	24,536
5	3729.3	26,815	6	3864.8	25,875	6	4094.2	24,425
5	3734.1	26,780	6	3868.2	25,852	5	4098.5	24,399
5	3736.7	26,762	5	3873.2	25,818	5	4099.1	24,396
5	3741.5	26,727	5	3879.0	25,780	6	4104.4	24,364
6	3743.7	26,712	5	3883.9	25,747	6	4128.2	24,224
6	3745.1	26,702	6	3885.7	25,735	6	4143.0	24,137
5	3747.9	26,682	5	3886.6	25,729	6	4150.2	24,095
5	3751.0	26,660	5d	3893.0	25,687	6	4157.4	24,053
5	3753.0	26,645	5d	3900.6	25,637	6	4175.5	23,949
6	3756.5	26,621	5	3907.5	25,592	6	4182.0	23,912
5	3760.3	26,594	5	3915.5	25,540	5	4193.7	23,845
6	3761.7	26,584	5	3923.5	25,487	6	4228.4	23,650
4d	3769.5	26,529	5d	3933.2	25,425	5	4235.9	23,608
5	3774.8	26,491	6	3940.7	25,376	5d	4265.0	23,447

An inspection of the map shews in several places an arrangement of the lines which suggests an harmonic relation of some sort between them: groups of lines where the successive lines are set at gradually increasing distances and have a gradually diminishing intensity. Such a group may be seen between the wave-lengths 3431·8 and 3450·7, another beginning at λ 3368·8.

In many cases we find that the distances between the lines of the group are in arithmetic progression, so that the wave-lengths of the group may be represented by a general formula $an^2 + bn + c$, the different lines of the group being deduced from this expression by giving n successive integral values.

Taking the series of strong lines of the spectrum between λ 3669·8 and λ 3547·7, we find the second differences of wave-length approximately constant, and equal to 0·443. Comparing then the observed wave-lengths with a series calculated to have their differences in arithmetic progression with a common difference, 0·443, we find—

Observed	Calculated	Difference
3669·8	3669·7	+·1
3659·1	3658·5	+·6
3647·7	3647·7	0
3637·4	3637·3	+·1
3627·6	3627·4	+·2
3618·1	3617·9	+·2
3609·0	3608·9	+·1
3600·4	3600·3	+·1
3592·0	3592·2	-·2
3584·3	3584·5	-·2
3577·3	3577·2	+·1
3570·4	3570·4	0
3564·2	3564·0	+·2
3557·8	3558·1	-·3
3552·3	3552·6	-·3
3547·7	3547·6	+·1

In many other groups a similar relation between the wave-lengths may be observed.

GROUP with second differences of wave-length equal to ·3.

Observed	Calculated	Difference
3544·9	3544·8	+·1
3540·7	3540·7	0
3536·7	3536·9	-·2
3533·6	3533·4	+·2
3530·0	3530·2	-·2
3527·3	3527·3	0

GROUP with second differences of wave-length equal to '133.

Observed	Calculated	Difference
3524·1	3524·1	0
...	3521·7	...
3519·0	3519·4	- '4
3517·2	3517·2	0
3515·2	3515·2	0
3513·3	3513·3	0
3511·6	3511·5	+ '1
3509·9	3509·8	+ '1

GROUP with second differences equal to '76.

Observed	Calculated	Difference
3507·6	3507·5	+ '1
3502·1	3502·0	+ '1
3497·2	3497·3	- '1
3493·3	3493·3	0
3489·5	3490·1	- '6
3488·0	3487·7	+ '3
3486·2	3486·0	+ '2

GROUP with second differences equal to '923. The first line may not belong to the group.

Observed	Calculated	Difference
3497·2	3497·9	- '7
...	3494·9	...
3492·3	3492·0	+ '3
3489·5	3489·2	+ '3
3486·2	3486·5	- '3
3483·9	3483·9	0
3481·4	3481·4	0
3479·1	3478·9	+ '2
3476·8	3476·5	+ '3
3474·0	3474·2	- '2
3471·9	3472·0	- '1
3469·6	3469·9	- '3
3467·7	3467·9	- '2
3465·8	3466·0	- '2
3464·1	3464·2	- '1
3462·5	3462·5	0
3460·9	3460·9	0
3459·4	3459·4	0
3458·2	3458·0	+ '2
...	3456·7	...
3455·4	3455·5	- '1

GROUP with second differences equal to $\cdot 3$.

Observed	Calculated	Difference
3497.2	3497.7	- .5
3488.0	3488.8	- .8
...	3480.2	...
3471.9	3471.9	0
3464.1	3463.9	+ .2
3455.4	3455.2	+ .2
3447.6	3447.8	- .2
...	3440.7	...
3433.5	3433.9	- .4
3427.7	3427.4	+ .3
3421.5	3421.2	+ .3
3415.4	3415.3	+ .1
3409.7	3409.7	0
3404.2	3404.4	- .2
3399.1	3399.4	- .3
3394.5	3394.7	- .2
3390.3	3390.3	0
3386.2	3386.2	0

GROUP with second differences of wave-length equal to $\cdot 2143$.

Observed	Calculated	Difference
3451.0	3450.8	+ .2
3447.6	3447.7	- .1
3444.7	3444.8	- .1
3442.3	3442.1	+ .2
3439.7	3439.6	+ .1
3437.4	3437.3	+ .1
3435.4	3435.3	+ .1
3433.5	3433.5	0
3431.8	3431.9	- .1

GROUP with second differences of wave-length equal to $\cdot 3$.

Observed	Calculated	Difference
3428.5	3428.8	- .3
...	3425.0	...
3421.5	3421.5	0
3418.3	3418.3	0
3415.4	3415.4	0
3412.8	3412.8	0

GROUP with second differences of wave-length equal to $\cdot 3$.

Observed	Calculated	Difference
3394.5	3394.2	+ .3
3390.3	3390.3	0
3386.2	3386.7	- .5
3383.3	3383.4	- .1
3380.2	3380.4	- .2
3377.6	3377.7	- .1
3375.4	3375.3	+ .1
3373.2	3373.2	0
3371.7	3371.4	+ .3
3370.1	3369.9	+ .2
3368.8	3368.7	+ .1

GROUP with second differences of wave-length equal to 1.467 .

Observed	Calculated	Difference
3349.1	3349.0	+ .1
3332.5	3332.8	- .3
3318.0	3318.1	- .1
3304.9	3304.9	0
3293.0	3293.1	- .1
3282.9	3282.8	+ .1
3273.7	3274.0	- .3
3266.4	3266.6	- .2
3260.7	3260.7	0
3256.4	3256.2	+ .2
3253.2	3253.1	+ .1
3252.0	3251.5	+ .5

GROUP with second differences of wave-length equal to $\cdot 322$.

Observed	Calculated	Difference
3086.7	3086.5	+ .2
3079.3	3080.0	- .7
3073.8	3073.9	- .1
3068.2	3068.1	+ .1
3063.3	3062.6	+ .7
3057.4	3057.4	0
3052.7	3052.6	+ .1
3048.3	3048.1	+ .2
3043.9	3043.9	0
3039.9	3040.0	- .1
3036.4	3036.4	0
3033.1	3033.2	- .1
3030.3	3030.3	0
3027.6	3027.7	- .1
3025.2	3025.4	- .2
3023.4	3023.4	0
3022.0	3021.8	+ .2
3020.9	3020.5	+ .4

GROUP with second differences of wave-length equal to $\cdot 783$.

Observed	Calculated	Difference
2893.5	2893.6	- .1
2882.5	2882.7	- .2
2871.9	2872.6	- .7
2863.3	2863.3	0
2854.9	2854.8	+ .1
2847.4	2847.1	+ .3
2840.1	2840.2	- .1
2834.0	2834.0	0
2828.7	2828.6	+ .1
2824.0	2824.0	0
2820.1	2820.2	- .1
2817.1	2817.2	- .1
2814.9	2815.0	- .1
2813.5	2813.5	0

GROUP with second differences of wave-length equal to $\cdot 457$.

Observed	Calculated	Difference
3020.9	3020.6	+ .3
...	2997.1	...
2992.9	2992.9	0
2980.2	2980.2	0
2968.0	2967.9	+ .1
2956.3	2956.1	+ .2
2945.2	2944.8	+ .4
2933.5	2933.9	- .4
2923.8	2923.5	+ .3
2913.5	2913.5	0
2903.7	2904.0	- .3
2894.2	2894.9	- .7
2886.3	2886.3	0
2878.3	2878.2	+ .1
2871.5	2870.5	...
2869.5		...
2863.3		0
2857.6	2856.5	...
2855.4		...
2850.2		0
2844.4	2844.3	+ .1
2838.8	2838.9	- .1
2834.0	2834.0	0
2829.8	2829.5	+ .3
2825.2	2825.5	- .3
2821.8	2821.9	- .1
2818.7	2818.8	- .1
2816.1	2816.1	0
2813.5	2813.9	- .4
2812.1	2812.2	- .1

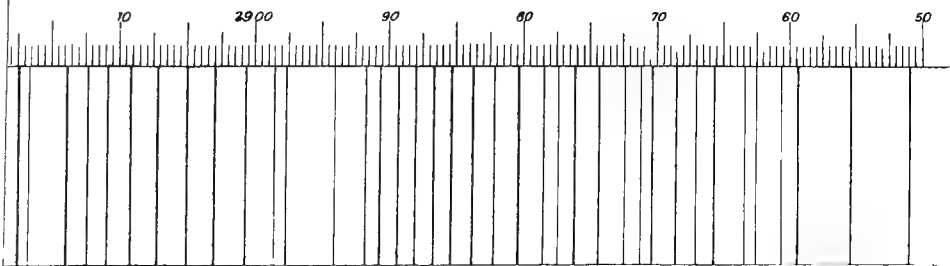
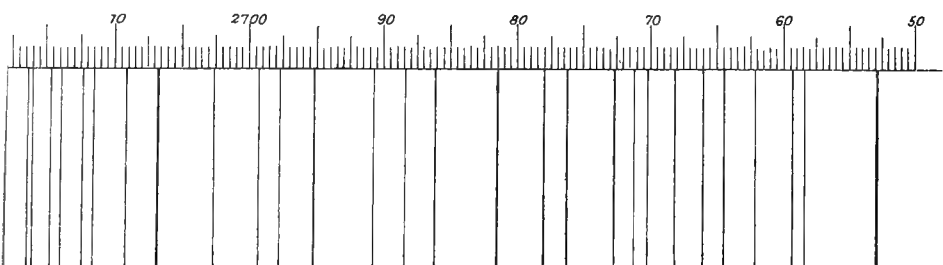
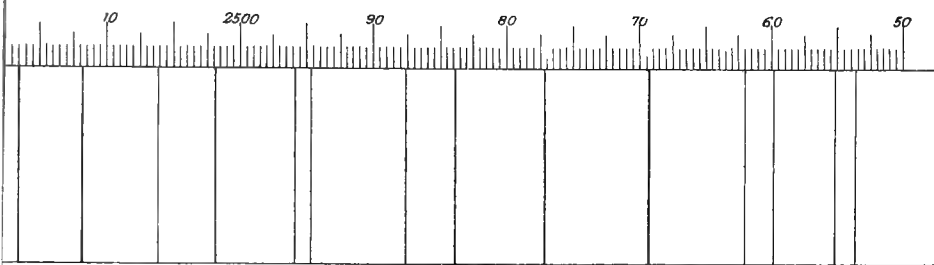
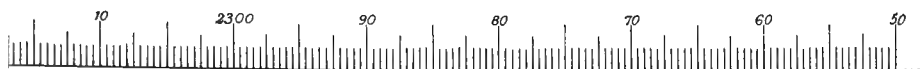
GROUP with second differences of wave-length equal to 2.4.

Observed	Calculated	Difference
3160.3	3160.5	- .2
3139.4	3139.7	- .3
3121.3	3121.3	0
3105.3	3105.3	0
3092.0	3091.7	+ .3
3081.0	3080.5	+ .5
3071.5	3071.7	- .2
3065.5	3065.3	+ .2

GROUP with second differences of wave-length equal to .522.

Observed	Calculated	Difference
3005.6	3005.4	+ .2
2991.7	2991.4	+ .3
2977.8	2977.9	- .1
2965.5	2965.0	+ .5
2952.5	2952.6	- .1
2940.6	2940.7	- .1
2929.9	2929.4	+ .5
2918.5	2918.6	- .1
2908.3	2908.3	0
2898.8 }	2898.5	...
2898.1 }		
2889.2	2889.2	0
2880.3	2880.4	- .1
2871.9	2872.1	- .2
2865.5 }	2864.4	...
2863.3 }		
2857.6	2857.2	+ .4
2850.7	2850.5	+ .2
2844.4	2844.3	+ .1
2838.8	2838.6	+ .2
2833.3	2833.4	- .1
2828.3	2828.8	- .5
2824.8	2824.7	+ .1
2821.2	2821.1	+ .1
2818.2	2818.2	0
2815.6	2815.7	- .1
2813.5	2813.7	- .2
2812.1	2812.2	- .1
2811.2	2811.2	0

Now, considering that the dispersion employed was that of a single prism, and that many of the lines are weak and many diffuse, the difference between the observed and calculated values falls in most of the cases above given within the limits of probable error. Indeed, one cause of the difficulty of obtaining very exact measurements of some of the lines arises from the overlapping of different groups, by which two or three lines fall nearly in the



SPECTRUM OF OXYHYDROGEN FLAME.

- 2608.

- 3426.

- 3472.

- 3546.

- H 8933.

- 3057.

- 3472.

- 2811.

same place, and produce a hazy band in the photograph which cannot be resolved into its constituent lines. We think, therefore, that the groups do actually follow the law above enunciated. M. Deslandres has observed the same law to hold in regard to inverse wave-lengths in the lines forming the bands of nitrogen, in those of A, B, and α , and in the groups of several spectra of compound gases; and has remarked that it is the law of sequence of the harmonics of solid rods. A. Herschel and Piazzi Smyth had previously noticed this law in the sequence of the rays in one of the bands of the spectrum of carbonic oxide.

While the work of photographing and measuring this spectrum was in progress we received from Dr Grünwald, Professor of Mathematics in the I. R. German Technical High School at Prague, a long list of lines which he had, on theoretical grounds, predicted would be found in the spectrum of water. The interest attaching to this prediction induced us to make a more extended and complete investigation of the spectrum than we had originally intended. Many of these predicted lines, though not all of them, agree closely with lines which we have recorded in the spectrum of the oxy-hydrogen flame; and in the weaker parts of the spectrum at either end, Dr Grünwald's list includes many of the strongest lines. His results have been (in part) published in the *Astronomische Nachrichten*. We are not at present in a position to discuss his theory, which is a far-reaching one, and will need to be tested at many points; but the coincidences between his predictions and the lines observed are very remarkable, and will, no doubt, attract the attention of many besides ourselves.

A map of the spectrum on a scale of inverse wave-lengths accompanies this Paper, and also an enlarged photograph which gives the general characters of the spectrum, though in the strongest part it has been over-exposed. The photograph includes the regions of the lines enumerated in Tables III to VI, and greater part of VII.

ON THE ULTRA-VIOLET SPECTRA OF THE ELEMENTS

PART III. COBALT AND NICKEL

[*Proceedings of the Royal Society*, Vol. XLIII. (1888), p. 430]

(*Abstract.*)

THE authors compare the results obtained by the Rutherford grating which they used in measuring the wave-lengths of the iron lines with those obtained with the larger Rowland's grating used for measuring the wave-lengths recorded in this paper, and find them closely concordant. They next compare the measures of wave-lengths of the cadmium lines obtained by them by means of a plane Rowland's grating and a goniometer with an 18-inch graduated circle with those obtained by Bell with a large concave grating of 20 feet focal length. The result of the comparison is that the plane grating gives measures which agree very closely with those given by the concave grating, while the former gives more light and is better for complicated spectra, such as those described in this paper, because the overlapping spectra of different orders are not all in focus together as they are when a concave grating is used.

The authors give a list of 580 ultra-violet lines of cobalt and 408 lines of nickel. They find a certain general resemblance of the two spectra, but no such exact correspondence as the close chemical relationship of the two metals would render probable. They point out that the coincidences of lines of the two metals are hardly, if at all, more in number than would have been the case if the distribution of the lines had been fortuitous. They give a map of each spectrum to the same scale as Ångström's normal solar spectrum.

ON THE ULTRA-VIOLET SPECTRA OF THE ELEMENTS
PART III. COBALT AND NICKEL

[*Philosophical Transactions of the Royal Society*,
Vol. 179 A (1888), pp. 231 sqq.]

IN our first communication to the Society on this subject we gave a reference map of the iron lines in the ultra-violet region, based on measurements of the wave-lengths of nearly a hundred of the principal lines. These measurements were made by means of a diffraction grating by Rutherfurd. Since that time we have obtained some of Rowland's fine gratings, having a much larger ruled surface, though a somewhat smaller number of lines to the inch, than the Rutherfurd grating. With larger gratings it was advantageous to use larger telescopes, and it was a matter of some interest to determine whether the improved appliances led to the same numerical values of the wave-lengths as before. In each case we determined the constant of the grating—that is, the distance between successive lines—by Ångström's scale. We had, for instance, measured the deviations by the Rutherfurd grating of several lines—namely, C, D, *b*, F, and H—for as many orders of spectra as we could on both sides of the collimator, and then calculated what must be the distance between the lines to produce these deviations, on the assumption that Ångström's wave-lengths of these lines were correct. We have since used the solar lines E, or the corresponding lines of the spectrum of the spark taken between iron terminals, for the purpose of gauging our gratings, because Ångström had bestowed the greatest pains in the measurement of the wave-lengths of these lines. Peirce and Bell have corrected Ångström's measures, but, for convenience in comparisons, we have retained the old scale. In order to make our numbers correspond to the new scale they must all be multiplied (according to Rowland) by 1.00016.

The first comparison of measurements with the different gratings was made with respect to the cadmium lines, which have frequently been used as lines of reference. Four pairs of photographs of the cadmium line No. 17 in Mascart's notation had given us the following wave-lengths:—

2748·58	. .	at 4th order.
2748·27	. .	„ „ „
2748·20	. .	„ 5th „
2748·16	. .	„ 6th „
Mean	.	2748·30

Six pairs taken with a Rowland grating and the same goniometer gave us—

2748·43	. .	at 3rd order.
2748·41	. .	„ 4th „
2748·50	. .	„ 5th „
2748·35	. .	„ 6th „
2748·41	. .	„ 7th „
2748·29	. .	„ 8th „
Mean	.	2748·40

Bell's* value of the wave-length of the same line is 2748·45. The photographs were all taken with a collimating eyepiece. Considering that the cadmium lines, though strong, are very diffuse, so that there is room for considerable error in estimating the centre of the photographic image, and that an error of 0·013 mm. in measuring the distance between the two images of the line on the photograph would make an error of 1" in the deviation, or very nearly ·03 in the value of the wave-length, the values above are fairly concordant. However, besides the difficulty of exact measurement arising from the ill-defined character of the cadmium lines, there is a source of error arising from the gratings themselves, and affecting both of them. It is that the two images of any given line, on the two sides of the normal to the grating, are not in focus at the same distance from the object-glass of the telescope. Hence, if the photographic plate is adjusted to the focus of a particular line when the grating is turned in one direction, it will not receive a sharp image of the same line when the grating is turned in the other direction.

With a collimating eyepiece it is comparatively easy to place the grating so that the normal to its plane may coincide with the axis of the collimator. Hence, fair measures of the wave-length of any line may be obtained from the deviation for that line, as measured on one side only of the normal. But, since every change of focus makes it necessary to take a fresh reading of the position of the grating when it is normal to the axis of the collimator, it is better, as a rule, because errors of reading thereby become of less consequence, to measure the angle between the two images, one on one side and the other on the other side of the normal. If this is done, the difficulty arising from difference of focus on the two sides must be faced, as any

* *Amer. Journ. Sci.*, Vol. xxxi, 1886, p. 429.

alterations of adjustment between the times of taking the pair of photographs would be wholly inadmissible.

Again, it seldom happens that a grating gives the two spectra of the same order equally bright. With one of our gratings the spectra of the 3rd and 5th orders are bright on one side only of the normal, while those of the 4th and 6th orders are bright on the other side only. Where faint lines were in question, therefore, we have used spectra of different orders on the two sides, and computed the wave-length by the formula

$$(m + n) \lambda = 4a \sin \frac{1}{2} (\alpha + \beta) \cos \frac{1}{2} (\alpha - \beta);$$

where m and n are the orders of the spectra employed, α and β the deviations of the ray from the normal. $(\alpha + \beta)$ is, of course, the angle directly measured; $(\alpha - \beta)$ has to be calculated from the reading of the instrument when the grating is normal to the axis of the collimator. As $\frac{1}{2} (\alpha - \beta)$ is always a small angle, any error in determining it will affect the value found for λ but little.

Measures of other cadmium lines gave the following results:—

No. of line	Rutherford grating		Rowland grating		Bell's value of λ
	No. of pairs of photographs	λ	No. of pairs of photographs	λ	
18	1	2572·95	5	2572·75	2572·95
22	2	2320·67	5	2320·92	2321·14
23	2	2312·66	5	2312·75	2312·83
24	2	2264·91	4	2264·64	2264·88
...	2	2240·18	...	...	...
25	1	2194·06	$7\frac{1}{2}$	2194·28	2193·98

Previous measures of lines Nos. 24 and 25, by interpolation between the copper lines of which the wave-lengths had been determined by Rutherford's grating, had given the values of λ 2265·0 and 2194·2.

Other cadmium lines, measured by Rowland's grating, gave the following results:—

No. of the line	No. of pairs of photographs	λ	Bell's value of λ
9	3	{ 3612·15 3609·75	3611·75 3609·39
10	3	{ 3467·03 3465·61	3466·70 3465·22
11	5	3403·08	3402·68
12	5	{ 3260·46 3252·08 3249·83	3260·12 3251·77 3249·40

The wave-lengths of this last group of lines are all too large by about 0.35 as compared with Bell's, and they seem to be affected by some common error, but whence it arises we do not know. Our measures of lines in the visible spectrum, where, of course, there are fewer sources of error, agree very closely with Bell's. Thus our measures of the blue lines gave the figures for λ 5085.26, 4799.40, and 4677.59, and these, when multiplied by the factor 1.00016, come very close indeed to Bell's numbers, which are 5086.09, 4800.15, and 4678.39. On the whole, we are inclined to think that a really good goniometer with a plane grating and a telescope of moderate dimensions, focal length 8 or 9 decimeters, will give extremely accurate wave-lengths, while the greater angular aperture of such a telescope gives it a considerable advantage in point of light over the concave grating used by Bell. The method of measuring wave-lengths by the coincidences of lines in spectra of different orders, for which a concave reflecting grating is admirably adapted, could not be easily applied to the ultra-violet spectra of cobalt and nickel, because the lines are so crowded that the overlapping of two or three spectra, all in focus together, would produce a complication which it would be nearly impossible to unravel, except by dispersing the spectra in a direction at right angles to the dispersion produced by the grating. The chromatic aberration of our quartz lenses is a positive advantage in dissipating the light of the spectra of those orders which are not under examination.

For the determination of the cobalt and nickel lines specimens of those metals were prepared so far spectroscopically pure that the spark between fragments of the cobalt shewed none of the characteristic strong lines of nickel, and the spark between pieces of the nickel shewed none of the characteristic strong lines of cobalt. As the metals after reduction were fused with an oxy-hydrogen blowpipe in lime crucibles, they were not free from all traces of other metals. For the arc lines much labour in the purification of the metals would have been wholly thrown away, because a variety of metals are present in the carbon electrodes as well as in the limestone used for crucibles. In the arc, therefore, we used samples sold as "pure," and identified the lines either by their coincidence with spark lines photographed at the same time through a part of the slit, or by their making their appearance, or being notably strengthened, on the introduction of the metal into the arc. The list of arc lines is much less complete than the list of spark lines, because weak lines in the arc are more easily overlooked in a photograph crowded with lines, and when noticed their origin is with difficulty identified. The wave-lengths of the spark and arc lines which were not measured directly by means of a grating were determined by interpolation from photographs of refraction spectra. In the highest region the copper lines were used as lines of reference in this interpolation. For the direct determination of the wave-lengths of the nickel lines about 170 photographs were taken, measured, and the results reduced; for the cobalt lines about 200. In many cases several

lines could be measured on the same plate, but we have rarely been satisfied without getting two or more independent measures of the deviation for each line, and in many cases the measures have been made in more than one order of the spectra. Owing to difference in the strength of the spectra on the two sides of the normal to the grating, it sometimes happened that faint lines appeared in one of a pair of photographs, that is on one side of the normal, but not on the other. In such cases, when the reading of the circle for the normal position of the grating (which is liable to vary with every adjustment of focus) could be accurately determined by the help of stronger lines, which could be measured in both photographs, the wave-lengths of the faint lines have been calculated from the deviation as measured on one side of the normal. Such a measurement, though it gives a valuable result, is plainly not quite independent.

From the close chemical relationship between cobalt and nickel we should have expected that their spectra would closely resemble one another. In regard to the large number of lines which they exhibit, they certainly resemble each other, and resemble iron; and the resemblance goes a little further, inasmuch as the lines of all three spectra are much more crowded in certain regions than in others, and the crowded regions are approximately the same for all three. But, beyond such a general resemblance, we have been unable to trace any definite correspondence in the spectra. The number of lines of cobalt which according to our measurements have wave-lengths identical with those of nickel lines is small, but in a record of 580 lines of cobalt and 400 of nickel it would be surprising if there were not many close coincidences, and, in fact, we note forty-six cases where lines of cobalt do not appear to differ in wave-length from lines of nickel by more than a tenth of a tenth-meter. Now, if the cobalt lines were uniformly distributed over the whole region mapped and the nickel lines distributed at random amongst them, it would be an even chance that twenty-six nickel lines would not be more than a tenth of a tenth-meter distant from the nearest cobalt lines. A glance at the map will, however, shew that the cobalt lines are by no means evenly distributed, and in the regions where they are most closely packed the nickel lines are also for the most part closely packed. Hence, the chance of merely accidental coincidences is very much greater than that above mentioned; and we find that in the region between the wave-lengths 2250 and 2550 the number of lines of the two metals, which, as measured, are not more than a tenth of a tenth-meter distant from one another is twenty-five, more than half the whole number of coincidences to that degree of approximation. On the whole we are unable to conclude that the coincidences are more than fortuitous. It should be observed that we have not yet had the opportunity of comparing the spectra of the two metals photographed on the same plate with high dispersion. On many of our plates the iron spark has been photographed simultaneously with the

spectrum of another metal, and we have noted on the table of wave-lengths the cases in which these photographs shew an unresolved coincidence between an iron line and a cobalt or nickel line. These photographs, however, have all been taken with a prismatic spectroscope, and it is probable that a higher dispersion might resolve some of these coincidences.

TABLE of Cobalt lines.

In the first two columns are given the intensities, 1 to 6, of the lines as observed in the spark and arc respectively, 1 being the most intense. In the third column are recorded the wave-lengths. A figure in the fourth column indicates that the wave-length against which it is placed was independently measured by means of a grating, and at the same time records the number of separate determinations combined in the given result.

Intensity		λ		Remarks
Spark	Arc			
6	...	2190.2	...	The wave-lengths of the lines in this region were obtained by interpolation between the copper lines photographed at the same time through a part of the slit
6	...	2191.9	...	
6	...	2193.1	...	
6	...	2198.2	...	
6	...	2205.7	...	
6	...	2214.1	...	
6	...	2215.9	...	
6	...	2219.6	...	
6	...	2229.5	...	
6	...	2231.5	...	
6	...	2234.4	...	
3	...	2244.8	...	
6	...	2253.2	...	
2	...	2256.4	...	
2	...	2259.7	...	A weak Ni line
2	...	2266.2	...	
6	...	2270.5	...	Also a Ni line
6	...	2272.0	...	
5	...	2273.3	...	A stronger Ni line
6	6	2274.2	...	
6	...	2275.1	...	
6	...	2275.9	...	
6	...	2278.1	...	
5	...	2280.1	...	
4	...	2281.5	...	
6	...	2281.9	...	
5	...	2283.1	...	
2d	2	2285.7	1	
6	5	2287.8	...	
6	6	2289.9	...	
6	6	2290.9	...	
3	4	2291.5	1	
3	2	2293.0	...	
5	4	3295.5	...	

TABLE of Cobalt lines—(continued).

Intensity		λ		Remarks
Spark	Arc			
5	5	2296.9		
6	6	2298.3		
4	6	2299.3		
5	5	2300.3		
5	4	2300.8		
6	...	2303.8		
6	...	2305.6	...	Also a Ni line
6	...	2306.4		
1d	2	2307.4	2	
6	6	2310.4		
1	3	2311.1	2	Also a Ni line
5	5	2312.1		
4	...	2313.1		
2	3	2313.5	2	Also a Ni line
2	5	2314.5	2	
6	4	2315.5	...	Also a Ni line
3	5	2316.8	...	Also a Ni line
6	...	2318.2		
6	4	2319.6		
6	5	2321.0	...	Also a Ni line
3	4	2324.0	2	Also a Ni line
3	5	2325.9	2	
3	4	2326.1	1	Also a Ni line
5	...	2327.3		
6	6	2328.7		
3	5	2330.0	1	Also a Ni line
6	6	2333.7		
3	4	2335.9	1	
5	...	2336.6	...	Also a Ni line
2	4	2337.6	1	
6	4	2338.4		
5	4	2338.8		
2	...	2340.8	1	Also a Ni line
3	...	2344.0	1	Also a Fe line
4	...	2344.3		
5	5	2345.2		
4	6	2346.2	...	Also a Ni line
6	5	2346.7		
3	5	2347.0	1	
5	...	2347.4		
6	...	2348.1		
5	5	2350.6	...	Also a Ni line and a Fe line
6	5	2351.5		
6	3	2352.1	1	
1	3	2353.0	2	
4	4	2357.7	1	
4	6	2360.0		
5	6	2360.2	2	
4	...	2360.3		
6	6	2360.8		
6	6	2361.2		
1	3	2363.3	2	
6	5	2366.6		

TABLE of Cobalt lines—(*continued*).

Intensity		λ		Remarks
Spark	Arc			
5	4	2370.1		
5	4	2371.3		
3	4	2371.5	2	
5	5	2372.6		
4	6	2374.8	2	Also a Fe line
1	2	2378.1	3	
6	6	2380.3		
2	4	2381.3	2	
5	...	2381.7	...	Also a Ni line
2	4	2382.9	2	
2	4	2385.9	2	
3	6	2386.1	1	
5	4	2388.3	2	A rather close double, very near a Fe line
1	6	2388.4		
3	4	2389.1		
6	4	2391.5		
4	4	2392.1	...	A weaker Ni line
4	6	2393.4		
4	4	2395.1		
1	5	2396.9	3	
4	5	2397.8	2	
6	{	2401.3	1	
6		2401.6	...	Also a Ni line
6	6	2402.4		
6	6	2403.3		
3	4	2403.8	3	
4	6	2404.0		
4	6	2405.1	1	
6	...	2406.9		
3	1 <i>d</i>	2407.1	3	
3	...	2407.8	2	
3	4	2408.3	2	
2	1	2411.2	2	
6	3	2412.2	2	Also a Ni line and an air line
3	4	2413.7	3	
5	2	2414.1		
5	2	2414.8	1	
3	...	2415.5		
4	...	2415.7	2	
3	5	2416.5	2	
3	3	2417.2	2	
3	4	2418.1	2	
1	6	2420.3	3	
6	6	2421.6		
6	4	2422.1		
3	6	2423.2	2	
4	1 <i>d</i>	2424.5	2	
5	6	2425.7	2	
3	...	2427.8	2	
5	5	2429.6	2	
6	...	2430.0		
1	1	2432.0	4	
5	2	2434.6	...	Close to a Si line

TABLE of Cobalt lines—(*continued*).

Intensity		λ		Remarks
Spark	Arc			
6	5	2435.8		
6	2	2436.2		
3	2	2436.5	3	
6 <i>d</i>	...	2437.9		
5	3	2438.5		
6 <i>d</i>	...	2439.7		
6	4	2440.6		
5	4	2441.2		
2	...	2442.0	3	
3	5	2443.3	2	
3	6	2445.6	3	
2	5	2447.3	2	Also a Fe line
4	...	2448.7	2	
2	...	2449.4	3	
6	6	2452.0		
6	...	2452.7		
6	5	2453.3		
6	...	2453.6		
6	2	2455.7		
3	...	2459.0	1	
6	3	2460.3		
6	...	2460.8		
1	4	2463.7	2	
2	...	2466.5	2	
6	6	2469.0		
6	3	2469.7		
6	2	2472.5		
6 <i>d</i>	6	2473.5		
6 <i>d</i>	...	2474.9		
6	...	2476.0		
6	3	2476.2		
6	...	2476.9		
4	...	2477.1	2	Also a Fe line
4	...	2477.8		
5	...	2478.6	...	Close to a carbon line
6	4	2483.2		
6	...	2484.1		
6	...	2484.4		
3	...	2484.8	1	
3	...	2485.9	3	Also a Fe line
6	...	2486.7		
6	...	2486.9		
3	3	2489.8	1	
6	3	2490.4		
6	5	2494.4		
6	4	2495.1		
6	2	2496.3		
3	3	2497.1	1	
4	...	2498.2	1	
5	3	2500.2		
5 <i>d</i>	6	2501.7		
6	3	2504.1		
1	1	2505.8	3	

TABLE of Cobalt lines—(continued).

Intensity		λ		Remarks
Spark	Arc			
4	4	2507.5	1	
6	...	2509.4		
1	1	2510.5	2	Also a Ni line
6	...	2511.4		
6	6	2511.7		
4	...	2516.9		
5	2	2517.3		
1	...	2519.3	2	
5	1	2520.7	1	
4	...	2522.5	1	Close to an air line
6	1	2524.2	1	Close to a Li line
2	...	2524.5	1	
2	2	2528.1	1	Also a Si line
3	3	2529.6	1	
6	1	2531.7		
2	...	2533.4	1	Close to a Fe line
5	4	2535.5	1	
6	4	2536.1		
5	6	2537.0		
3	{	2540.2	1	
2		2541.5	1	
6		2543.9		
6		2544.2		
5	4	2544.6		
6	3	2545.7		
2	...	2546.3	1	
6	4	2548.9		
6d	4	2549.7	...	Also a Fe line
4	...	2550.1	...	Also a Fe line
4	...	2552.2		
6	4	2552.7	...	Also a Ni line
6	4	2553.1		
3	...	2556.3	1	
4	4	2556.9	1	
2	6	2558.9	1	
3	6	2559.6	1	
6	1	2561.7		
1	6	2563.6	1	
6	...	2565.0		
6	3	2567.0		
3	...	2569.3	1	
6	4	2571.9		
6	4	2573.1		
3	5	2574.4	1	Also an Al line
1	5	2579.8	1	Also a Ni line and close to an air line
3	6	2581.7	1	
5	...	2582.6	1	
6	5	2584.8		
2	6	2586.8	...	Also a Ni line
6	6	2592.9		
6	6	2598.8	...	Also a Fe line, or close to it, and close to an air line
6	5	2600.3		
5	5	2603.9		

TABLE of Cobalt lines—(continued).

Intensity		λ		Remarks
Spark	Arc			
4	4	2605.2		
6	5	2605.3		
4	...	2613.0		
3	6	2613.8		
4	2	2618.5		
4	6	2619.3		
6d	4	2621.7		
6d	6	2626.6		
6	3	2627.3		
6d	...	2628.4	...	A Ni line, doubtful Co line
3	6	2631.9		
5	...	2634.5		
6d	6	2642.7		
6	6	2644.4		
5	3	2646.1		
2	1	2648.4		
3	...	2653.3		
2	6	2662.7	1	
5	6	2669.7	1	
6	...	2670.1	...	Also a Ni line
3d	4	2675.4		
5	...	2677.4		
6	4	2679.0		
5	...	2679.8		
6	...	2681.5		
3d	...	2684.0	1	Also a Ni line
5	...	2689.2	1	
5	...	2692.5	1	
2	6	2694.1	2	
6	3	2695.3	1	
6	...	2695.9		
6	...	2696.0		
6	...	2696.4	1	
4	...	2701.9	1	
4d	...	2706.2	1	Also a Fe line
6d	...	2706.9	1	Also a Fe line
5d	...	2707.4	1	
6	6	2708.6	1	Also a Fe line
3	...	2713.9	3	Very close to a Fe line
6	...	2714.5		
5	3	2715.3		
4	...	2720.6	1	Very close to a Fe line
4d	...	2727.5		
4d	...	2728.8		
6	6	2730.7		
6	...	2732.6		
5d	...	2734.3		
6	...	2738.6		
5	5	2744.7		
6	6	2757.1		
6	5	2761.0	1	
5	4	2763.9		
5	4	2766.0		

TABLE of Cobalt lines—(*continued*).

Intensity		λ		Remarks
Spark	Arc			
5	...	2766.5	1	
4	6	2768.6	1	
5 <i>d</i>	6	2774.8	...	Also a diffuse line in the Ni spark
2	...	2775.7	1	
6	6	2778.5		
5 <i>d</i>	...	2785.2		
5 <i>d</i>	...	2785.7		
5 <i>d</i>	...	2786.9	1	
6	...	2789.1	...	Also a Fe line
3	...	2793.4		
6	...	2795.8		
6	...	2796.3		
6	...	2796.6		
6	6	2798.4		
5 <i>d</i>	...	2801.7	1	
6	5	2803.3	...	Also a Fe line
4	...	2806.7	2	Also a Fe line
3	...	2810.3	4	
4	3	2815.2	1	
6 <i>d</i>	...	2815.8		
6	6	2818.3		
6	6	2819.4		
6 <i>d</i>	5	2821.1		
5 <i>d</i>	...	2822.7		
6	...	2823.2	1	
2	2	2824.5	5	
3	...	2834.3	1	
6	6	2836.7		
6	...	2845.2		
5 <i>d</i>	...	2847.9	...	Also a Fe line
6	5	2849.8		
6	5	2862.2		
6	...	2865.1	...	Also a Ni arc line
2	...	2870.4	1	Very close to a Fe line
6 <i>d</i>	...	2879.9		
6	3	2881.3	1	
6 <i>d</i>	...	2883.1		
5	4	2886.0		
2	6	2890.0		
5 <i>d</i>	...	2897.5		
6	3	2899.3		
6	5	2906.5		
3 <i>d</i>	...	2918.1		
6	6	2927.2		
6	6	2929.0		
2 <i>d</i>	...	2930.0		
2 <i>d</i>	2	2942.5	1	
1 <i>d</i>	...	2954.1	1	
6 <i>d</i>	...	2971.2		
6 <i>d</i>	6	2983.3		
3	3	2986.5		
3	3	2989.1		
6	...	2994.7		

TABLE of Cobalt lines—(continued).

Intensity		λ		Remarks
Spark	Arc			
6	5	3000.1		
6 <i>d</i>	6	3008.5		
6	5	3010.3		
4	4	3013.2		
6	6	3015.2		
3	...	3017.0	...	Very close to a Fe line
2	{ 5	3033.8		
	{ 5	3034.0		
6	{ 5	3042.2		
3	{ 3	3043.6		
3	{ 3	3048.6		
4	{ 3	3050.6	...	Very close to a Ni line
6	{ 6	3059.6		
2	{ 3	3061.4		
6	{ 5	3063.0		
6	{ 4	3064.0		
2	{ 6	3071.8		
	{ 2	3072.0		
6	{ 6	3073.4		
6	{ 6	3078.9		
3	{ 3	3082.1		
2	{ 2	3086.3		
4	{ 4	3089.0		
4	{ 3	3097.6		
6	{ ...	3101.8		
5	{ 5	3103.3		
6	{ 6	3109.0		
6	{ 6	3109.5		
5	{ 5	3113.0		
2	{ 2	3121.1	1	
6	{ 6	3126.7		
4	{ 6	3130.4	1	
3	{ 2	3136.8	1	
3	{ 3	3139.5	1	
3	{ 3	3146.6	1	
5	{ 4	3148.9		
6	{ 6	3152.3		
2	{ 3	3154.2	1	
3	{ 3	3158.2	1	
5	{ 5	3159.2		
6	{ 6	3161.3		
6	{ 6	3164.3		
5	{ 5	3169.5		
6	{ 4	3174.8		
4	{ 5	3176.6	1	Out of focus in photograph with grating
5	{ 5	3181.7		
5	{ 5	3188.0		
6	{ 6	3210.1		
5	{ 4	3218.7		
6	{ 6	3226.5		
5	{ 4	3232.4	1	
5	{ 5	3235.2		
5	{ 4	3236.7	1	

TABLE of Cobalt lines—(continued).

Intensity		λ		Remarks
Spark	Arc			
4	5	3243.4	1	Also a Fe line
3	...	3246.7	1	Also a Fe line
6	5	3249.6		
4	4	3253.7	1	
4	5	3260.1	1	
6	5	3261.7		
6	...	3262.7		
5d	5	3264.4		
5	6	3271.3		
6	6	3276.0		
6	4	3277.2		
5	6	3278.5		
2	3	3282.9	1	
6	...	3284.2		
5	5	3286.6		
6	...	3294.2	1	
6	6	3303.2		
6	6	3306.5	1	
6	6	3308.2		
5	...	3309.1		
5	5	3311.7	1	Also a Ni line
4	5	3313.6	4	
3	4	3319.0	1	
4	4	3321.7	3	Also a Ni line
5	5	3324.8	3	
5	5	3326.4	3	
6	6	3329.0	1	
2	1	3333.6	4	
5	5	3339.3	2	
6	5	3340.2	1	
6	5 {	3340.8	2	
5	5	3342.2	2	
5	5	3346.4	1	
5	5	3347.7	1	
6	5	3348.9	1	
4	...	3352.3	4	
2	1	3353.9	4	
6	3	3360.8	1	Also a Ni line
6	6	3362.3		
3	1	3366.6	5	
4	4	3370.4	4	
6	5d	3376.6	1	
5	6	3378.0	2	
6	1	3380.0	2	Also a Ni line
4	2	3384.7	3	
6	...	3387.1	3	
3	1	3387.6	5	
6	1	3394.2	1	
3	1	3394.8	5	
2	1	3404.5	4	Also a Ni line and in OH flame with CoCl
6	...	3406.1		
3	1	3408.6	3	In OH flame with CoCl ₂
2	1 {	3411.7	3	In OH flame with CoCl ₂
3	1	3412.0	3	

TABLE of Cobalt lines—(continued).

Intensity		λ		Remarks
Spark	Arc			
...	2	3414.2	3	
6	...	3415.2	3	
4	2	3416.5	3	In OH flame with CoCl_2
4d	3	3423.2	3	Also a Ni line
4	{	3430.9	3	In OH flame with CoCl_2
5		3431.3		
3		3432.4	4	In OH flame with CoCl_2
3	1	3432.9	1	Also a Ni line
5d	4	3436.8	...	Also a Ni line
...	6	3438.2		
6	3	3442.3	3	
3	3	3443.0	3	In OH flame with CoCl_2
4	3	3445.7	2	Also a Ni line and in OH flame with CoCl_2
3	{	3448.6	3	In OH flame with CoCl_2
5		3448.9	2	
2		3452.9	3	Also a Ni line and in OH flame with CoCl_2
4	3	3454.6	2	
5	4	3460.6	2	
2	2	3462.2	3	In OH flame with CoCl_2
2	1	3465.2	5	Also a Ni line and in OH flame with CoCl_2 and a Fe line
1	1	3473.4	5	In OH flame with CoCl_2
6	2	3476.0	1	
6	5	3478.0		
3	1	3482.7	2	In OH flame with CoCl_2
4	4	3484.7	2	
1	1	3488.8	5	In OH flame with CoCl_2
5	4	3490.6	2	
3	1	3495.1	4	In OH flame with CoCl_2
5	3	3496.0	3	
4	{	3501.0	2	
1		3501.6	3	In OH flame with CoCl_2
5		3502.0	2	
6	...	3503.4		
1	2	3505.6	3	In OH flame with CoCl_2
4	{	3509.3	5	In OH flame with CoCl_2
6		3509.7	4	Also a Ni line
4		3512.0	3	In OH flame with CoCl_2
3	2	3517.7	5	
5	3	3519.5	2	
3	2	3520.9	4	Also a Fe line
3	3	3522.9	4	In OH flame with CoCl_2
4	3	3526.3	4	
6	4	3528.4	3	In OH flame with CoCl_2
3	1	3529.3	4	Also a Ni line
4	3	3532.8	4	In OH flame with CoCl_2 and a Fe line
4	5	3542.8	3	
6	6	3544.7	1	
6	6	3548.0		
4	3	3550.1	3	
6	6	3552.4	1	
2	3	3560.5	3	In OH flame with CoCl_2
6	...	3562.3		

TABLE of Cobalt lines—(continued).

Intensity		λ		Remarks
Spark	Arc			
3	1	3564.5	2	In OH flame with CoCl_2 and close to a Fe line
1	1	3568.9	3	In OH flame with CoCl_2
1	1	3574.5	2	In OH flame with CoCl_2
		3574.9	2	
6	5	3577.4	1	
3	2	3584.7	3	Also a Fe line
1	2	3586.7	3	
3	1	3594.4	3	Observed in OH flame with CoCl_2
3	1	3601.6	3	Observed in OH flame with CoCl_2 and close to a Ni line
3	2	3605.0	4	Also a Fe line
6	6	3611.3	4	
6	6	3614.8		
3	1	3627.3	4	Observed in OH flame with CoCl_2
6	6	3632.2	4	
4	6	3634.2	2	
6	6	3636.1	1	
6	5	3638.9	3	
6	6	3641.1	1	
5	5	3642.7	3	
6	...	3648.8	3	
6	...	3654.0	1	
6	5	3656.1	1	
3	4d	3661.6	3	
6	...	3680.8	3	
3	2	3682.5	3	
6	6	3690.2	1	
		3692.4	1	
3	3	3692.8	3	
3	6	3701.7	4	
2	1	3703.5	6	Observed in OH flame with CoCl_2
6	...	3711.6		
5	5	3729.8	4	
4	5	3731.8	4	
6	5	3732.8	2	
6	...	3735.2	2	
1	...	3745.8	2	Observed in OH flame with CoCl_2
6	...	3753.9	2	Arc lines obscured in this region by bands of cyanogen
6	...	3769.7		
6	5	3774.0		
6	5	3777.0		
6	5	3807.3		
6	...	3815.1	2	A Fe line here
6	...	3815.7	2	
6	...	3830.3		
2	4	3841.4	7	Observed in OH flame with CoCl_2
1	2	3844.8	9	Observed in OH flame with CoCl_2
4	...	3860.5	5	Arc obscured by bands of cyanogen
2	1	3872.4	4	Observed in OH flame with CoCl_2
3		3873.2	5	
6	5	3876.1	4	
3	1	3881.0	5	
6	...	3884.0		

TABLE of Cobalt lines—(*continued*).

Intensity		λ		Remarks
Spark	Arc			
1	1	3893.4	4	Observed in OH flame with CoCl_2
5	...	3894.3	2	
6	4	3905.2		
6	4	3909.0	...	Observed in OH flame with CoCl_2
6	6	3916.2		
3	5	3935.5	1	Observed in OH flame with CoCl_2
6	3	3940.9	1	Observed in OH flame with CoCl_2
6	6	3944.9	1	
6	6	3952.4	1	
6	6	3955.7	1	
6	4	3957.7	1	
6	...	3968.8	1	
...	5	3974.1		
2	2	3978.7	...	Observed in OH flame with CoCl_2
...	6	3987.1		
...	5	3990.2		
...	5	3991.4		
1	2	3994.7	3	In OH flame with CoCl_2
6	1	3997.3	2	

TABLE of Nickel lines.

In the first two columns are given the intensities, 1 to 6, of the lines as observed in the spark and arc respectively, 1 being the most intense. In the third column are recorded the wave-lengths. A figure in the fourth column indicates that the wave-length against which it is placed was directly measured by means of a grating, and the figure records the number of separate determinations combined in the given result.

Intensity		λ		Remarks
Spark	Arc			
4	3	2173.8	1	
4	3	2174.4		
5	...	2176.0		
5	...	2176.7		
6	...	2179.4		
4	...	2179.9		
6	3	2182.8		
3	3	2184.2	1	
3	6	2185.0		
5	6	2188.2		
6	4	2190.0		
6	4	2190.6		

TABLE of Nickel lines—(continued).

Intensity		λ		Remarks
Spark	Arc			
6	...	2193.2		
6d	3	2197.2		
6d	...	2198.0		
5	4	2198.4		
2	4	2200.8	1	
6d	...	2203.0		
3d	3	2205.2		
2	2	2206.1	1	
2d	3	2209.8	1	
4	4	2210.5	...	Also a Fe line
6	5	2211.4	...	Also a Fe line
4	5	2212.5	1	
2	1	2215.8	2	A weak line in Co
3	5	2216.0		
5	5	2217.4	2	
6	...	2219.0		
3	6	2219.8	2	
5	...	2220.6		
6	5	2221.3		
6	...	2221.7		
3	2	2222.3	2	
3	...	2223.8	1	
3	2	2224.3	2	
6	...	2225.3	...	Also a Fe line
3	3	2225.8	2	
6	...	2226.7		
6	2	2227.2	...	Also a Fe line
4d	3	2229.6	...	A weak line in Co; also a Fe line
6	...	2231.2		
5	...	2233.5	} 1	The mean of this pair was measured by the grating
6	...	2235.5		
6d	...	2237.6		
6d	...	2238.2		
6d	...	2239.8		
E	...	2241.2		
6	5	2242.2	1	A weak line in Fe
6d	2	2244.4		
6d	...	2245.9	1	
5	...	2246.6	1	
6	...	2247.4		
6	4	2248.8	...	Also a Fe line
6	...	2249.2		
6	...	2250.2		
6	6	2250.5	...	Also a Fe line
6	6	2251.1	...	Also a Fe line
6	4	2251.4		
6	...	2252.6		
1d	2	2253.5	2	
6	...	2253.9		
3	3	2254.7	1	
3	5	2255.7	1	
4	3	2257.6		
5	...	2258.9		

TABLE of Nickel lines—(continued).

Intensity		λ		Remarks
Spark	Arc			
6	3	2259.4		
6	...	2260.3	...	Also a Fe line
6	4	2261.1		
6	6	2262.6		
...	4	2263.1	...	A weak Fe line; ? if Ni
2	1	2264.1	2	Also a Fe line
5	...	2264.8	...	Also a Fe line
6	5	2266.1	...	A stronger line in Co
6	3	2269.1	1	
1d	1	2269.9	2	
6	...	2270.3		
6	5	2271.1		
6	...	2272.3		
6	6	2273.2	...	Also a Co line
3	3	2274.1	...	A weak Co line
4	5	2275.0	...	A weak Co line and a Fe line
5	4	2275.7	1	Also a Fe line
...	5	2276.3		
3	6	2277.0	2	
3	4	2277.8		
2d	3	2278.4	1	
6	1	2279.2		
6d	...	2280.6		
6	6	2283.7		
6	...	2284.8		
2	3	2286.8	1	
2	6	2287.4	1	
4	4	2289.6		
6	...	2290.7		
6	6	2292.7		
6	...	2295.3	1	
2	...	2296.2	1	
3	...	2296.7	2	{ The mean of this pair was measured by the grating
3	6	2297.1		
3d	6	2298.0	4	
3	...	2299.2	4	
3	...	2299.8	4	
6	...	2301.5	1	
2	...	2302.0	4	
2	...	2302.5	5	
3	4	2303.3	2	
3	...	2304.8	2	
6	...	2305.7	...	Also a Co line
3	6	2308.1	2	
5d	3	2310.6	1	
6	...	2311.2	...	Also a Co line
4	3	2311.8	3	
3	...	2312.5	3	
6	3	2313.4		
5	3	2313.6	1	Also a Co line and a Fe line
1d	3	2315.6	3	Also a Co line
6	3	2316.8	...	Also a Co line
3	...	2318.0	2	

TABLE of Nickel lines—(continued).

Intensity		λ		Remarks
Spark	Arc			
3	3	2319.3	3	
4	2	2321.0	2	Also a Co line
6	5	2321.6		
6	3	2322.3		
6d	...	2323.3		
6d	...	2324.0	...	Also a Co line
4	2	2325.5		
2	3	2326.0	2	Also a Co line
4	2	2329.6	2	
6	...	2330.1	...	Also a Co line
2	6	2334.1	3	
3d	6	2336.2	3	
6	3	2336.6	...	Also a Co line
6	5	2337.1		
2	...	2340.7	3	Also a Co line
4	6	2343.0	3	
6	...	2343.5		
2	3	2344.7	3	Also a Fe line
6	...	2345.0		
6	4	2346.2	...	Also a Co line
6	4	2347.6	1	
6d	6	2349.8	...	Also a weak Fe line
6	6	2350.5	...	Also a Co line
3	3	2355.9	2	
6	3	2358.5	1	
4	6	2366.1	1	Also a Fe line
4	5	2367.0	1	
5	6	2368.9		
4	...	2369.5		
6	6	2370.9		
2	4	2375.0	2	
6	3	2375.6		
6	6	2378.6		
2	5	2381.8	...	Also a Co line and a Fe line
6	3	2386.3	1	
3	4	2387.5	1	
4	6	2388.5	1	Also a Fe line
6	6	2388.7		
6	6	2392.0	...	Also a Co line
4	3	2392.6		
2	2	2394.0	1	Also a Fe line
2	2	2394.3	1	
6	3	2394.7	...	Also a Fe line
6	...	2397.2		
6	...	2400.1	1	Also a Fe line
6	3	2401.7	...	Also a Co line
6	6	2404.8	1	
6	3	2412.1	1	Also a Co line and an air line
5	3	2412.8		
1d	2	2416.0	2	
6	3	2419.0		
6	2	2420.8		
6	3	2423.4		

TABLE of Nickel lines—(*continued*).

Intensity		λ		Remarks
Spark	Arc			
6	...	2426.8		
6	...	2431.2		
4	...	2433.2	...	Also a Fe line
6	3	2433.9	...	Also a Fe line
1d	3	2437.5	2	
6	1	2441.5	...	Also a Fe line
5	...	2448.1		
6	2	2453.7		
4	6	2455.4		
6	2	2471.8	...	Also a Fe line
2	3	2472.8	1	Also a Fe line
6	6	2476.6		
3d	3	2483.6	1	
6	6	2496.9		
3	...	2505.9	3	Also a Co line
6	...	2509.6	2	
1	2	2510.6	3	Also a Co line
6	6	2520.0		
6	...	2524.1	...	Close to a Si line
6	3	2539.5		
5	...	2543.2	1	Also a Fe line
3	3	2545.4	3	
6	6	2549.1	2	
6d	4	2552.6	1	Also a Co line
4	...	2554.7	1	
6	...	2557.5		
4	5	2559.8	1	
4d	...	2565.7	1	
6	6	2568.2	1	
6	6	2571.7		
4	4	2575.7		
6	6	2579.9	...	Also a Co line
4	...	2583.5		
5	...	2584.4	1	
6	6	2586.7	...	Also a Co line
5	...	2593.1	...	Also a Fe line
6	...	2600.8	1	
6	...	2606.1	1	Also a Fe line
6	...	2606.7	...	Also a Fe line
3	...	2609.6	1	
3	...	2614.9	1	Also a Fe line
6	...	2626.3	1	
6	...	2628.4	...	A doubtful Co line
6	...	2632.4	1	
6	...	2636.8		
3	...	2639.5	1	Also a Fe line
6	...	2641.0		
6	...	2643.4		
3	3	2646.8	1	
6	6	2648.6		
3	6	2655.6	1	
5	5	2659.5	1	
6	...	2664.9		

TABLE of Nickel lines—(*continued*).

Intensity		λ		Remarks
Spark	Arc			
5	...	2670.0	...	Also a Co line and a Fe line
6	...	2672.1		
5	...	2674.4		
3	...	2678.8		
2	...	2684.0	...	Also a Co line
6	...	2690.2		
6	6	2700.4		
5	6	2701.2	...	Also a weak line of Fe
4	4	2708.3		
4	...	2758.7	1	
6	...	2760.4		
4d	...	2774.7	2	Also a diffuse line in the Co spark
2	3	2805.0	3	
6d	...	2806.0		
6	...	2807.8		
3	1	2820.8		
6	...	2823.9		
2	...	2863.3	1	
...	3	2865.1	...	Also a line in the Co spark } These are perhaps air lines
6d	...	2880.9	...	
6d	...	2882.2	...	
6	...	2889.1	...	
6	...	2898.8		
5	...	2900.6		
5	3	2906.9		
2	2	2913.2	1	
6d	...	2918.8	/	
3d	...	2928.4	1	Also a Fe line
6	...	2934.3		
2d	...	2936.3	1	Also a Fe line
6	6	2938.7	...	
2	1	2943.5	1	Also a Fe line
4	...	2947.1	1	
5d	...	2954.5		
6	...	2957.8		
5d	...	2968.7		
3	3	2981.2	3	Also a weak Fe line
4	3	2983.6	3	
5d	...	2987.7	3	
6	...	2988.0		
3	2	2992.2	3	
3	3	2994.1	3	Also a Fe line
2	2	3002.1	4	
2	2	3003.2	4	
1	1	3011.5	6	
3	...	3018.8	4	
4	4	3031.4		
2	2	3037.5	5	
4	4	3044.5	5	Also a Fe line
2	2	3050.4	4	
2	3	3053.9	6	
2	...	3057.2	6	Also a Fe line
3	3	3064.2	4	

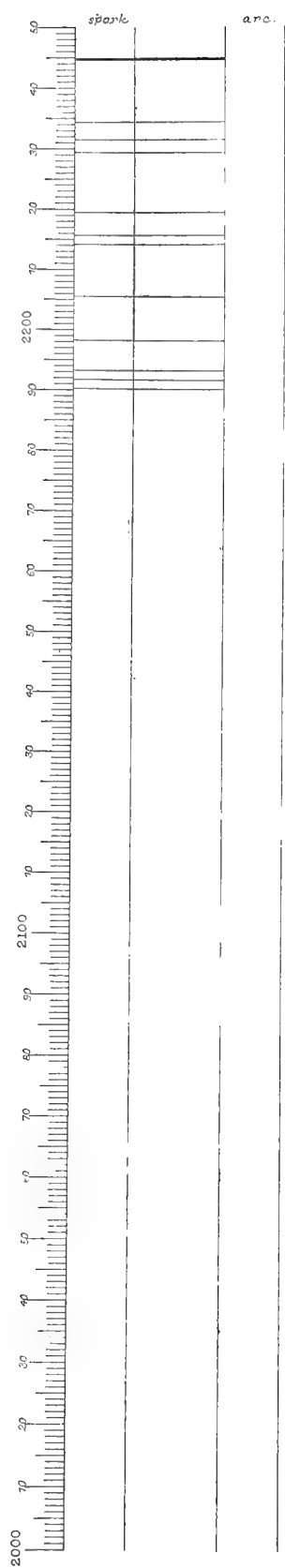
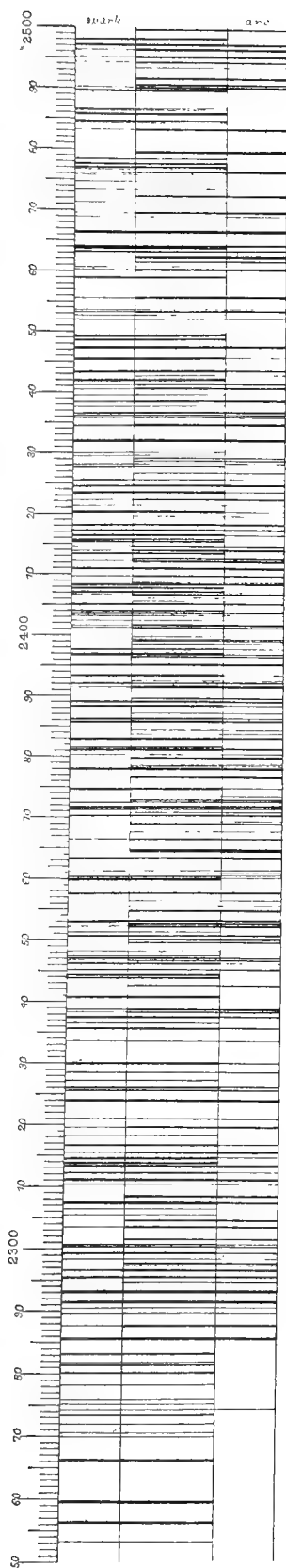
TABLE of Nickel lines—(*continued*).

Intensity		λ		Remarks
Spark	Arc			
3	3	3080.3	4	
2	...	3086.6	4	
4	...	3096.6	6	
4	...	3098.6	5	
3	3	3101.1	5	
2	2	3101.4	5	
5	3	3105.0	5	Also a Fe line
5	4	3113.7	6	
1	1	3133.6	6	Also a Fe line
6	6	3134.0	4	
5	4	3145.5	2	
5 <i>d</i>	5	3158.9	1	
3 <i>d</i>	3	3179.2	2	
6	...	3181.2	1	
6	6	3182.6	1	Also a Fe line
6	3	3183.8	1	
6	4	3194.9	4	
3	3	3196.6	4	Also a Fe line
6	...	3201.5	4	
...	6	3212.3		
5	...	3213.7	3	Also a Fe line
6	...	3216.0		
6	6	3216.6		
5	...	3217.4	3	
5	5	3221.1	3	
4	4	3224.6	3	
6	6	3226.3	3	
2	1	3232.6	1	Also a Fe line
3	3	3234.2	3	
3	3	3242.6	3	
6	6	3247.8		
4	5	3250.1	3	
6	6	3270.6	1	Also a Fe line
6	...	3274.4		
5	4	3282.2	6	
6	...	3290.1	6	
5	6	3311.8	3	Also a Co line
6	...	3312.4	3	
3	3	3315.1	4	
3	3	3319.7	4	
3	4	3321.6	4	Also a Co line
5	...	3349.8	3	
6	5	3358.1	2	
3	2	3360.9	3	Also a Co line
5	3	3361.0	3	
4	4	3365.1	3	
4	4	3365.5	3	
6	2	3367.2	1	In explosions of O, H with Ni
2	3	3368.9	4	Also a Fe line
3	4	3371.3	4	
3	3	3373.3	3	
6	4	3373.6	2	
4	4	3374.0	4	

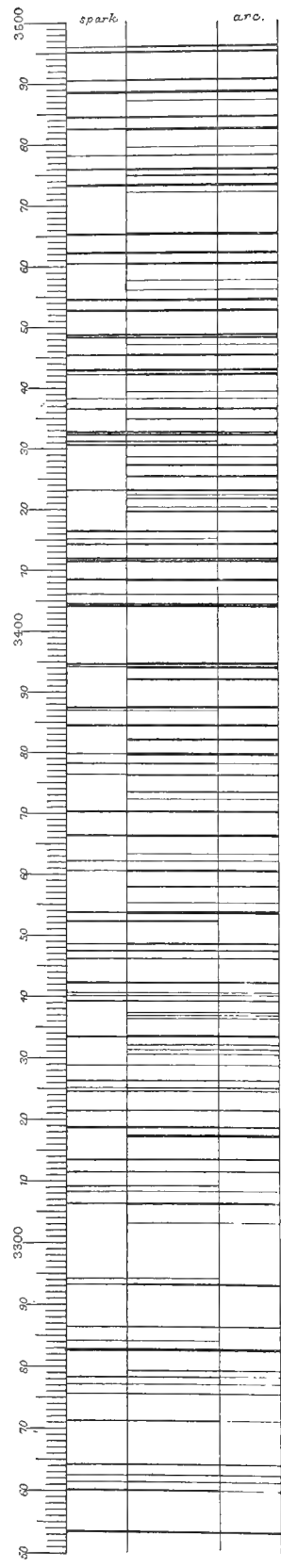
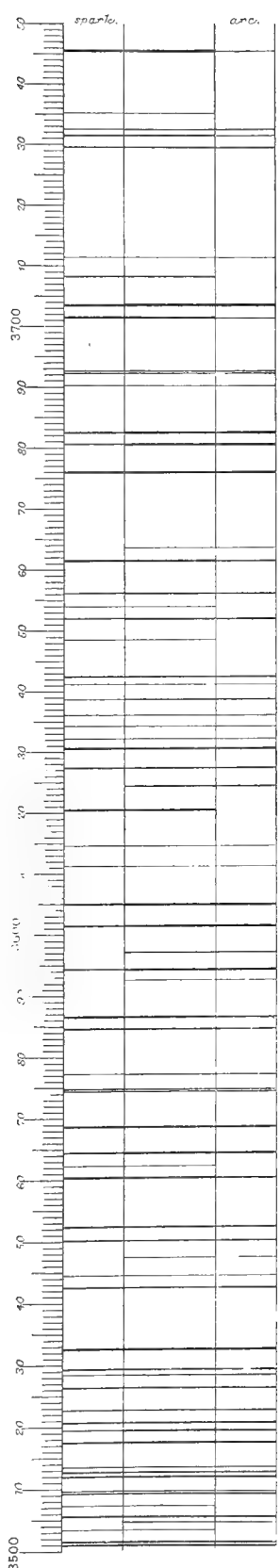
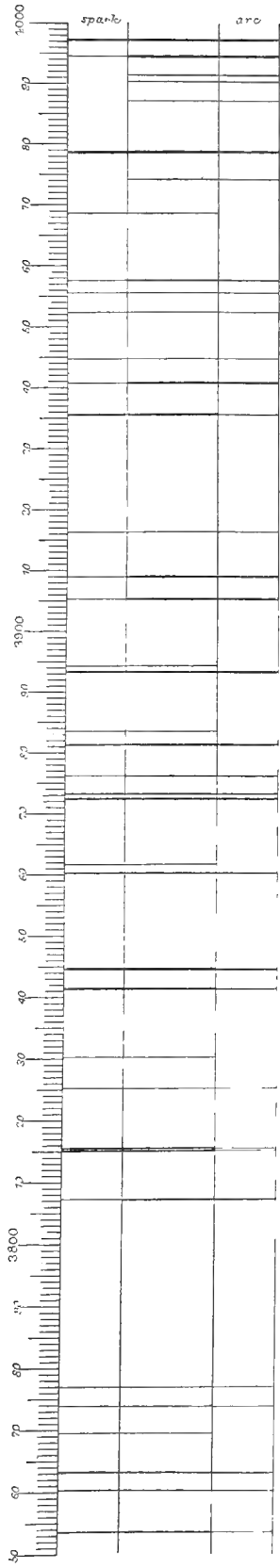
TABLE of Nickel lines—(continued).

Intensity		λ		Remarks
Spark	Arc			
1	1	3380.0	4	Also a Co line
2	2	3390.4	3	
2	2	3392.4	4	
6	5	3400.5	2	
6	...	3402.8	2	Also a Co line
5	6	3404.5	2	
3	3	3406.6	3	
6	5	3409.0	2	
2	2	3412.9	3	In explosions of O, H with Ni
4	1	3413.4	2	
1	2	3413.8	4	
6	6	3420.6	1	
1	2	3423.1	4	Also a diffuse Co line
1	1	3433.0	4	Also a Co line
2	2	3436.7	5	Also a Co line
6	...	3441.6		
1	1	3445.7	4	Also a Co line and in explosions of H, O with [Ni]
1	4	3452.3	3	
5	4	3452.9	2	In explosions of O, H with Ni
4	4	3453.5	3	In explosions of O, H with Ni
5d	2	3457.7	...	
1	1	3457.9	6	In explosions of O, H with Ni
1	1	3461.1	5	
3	2	3465.1	4	Also a Co line
5	5	3466.8	2	
5	4	3468.9	4	
5d	6	3470.8	3	
2	2	3471.9	4	
2	2	3483.1	4	
5	5	3485.2	2	
1	1	3492.3	3	In explosions of O, H with Ni
2	2	3500.0	3	
5	4	3501.8		
6	5	3505.9		
6	6	3507.3		
1	1	3509.7	4	Also a Co line and in explosions of O, H with [Ni]
2	...	3513.3	4	Also a Fe line
1	1	3514.4	4	In explosions of O, H with Ni
6	...	3518.0		
3	3	3519.1	1	
1	1	3523.9	2	In explosions of O, H with Ni
5	...	3526.0		
5	6	3527.1	1	Here is a series of fine closely-set lines Also a Co line
6	5	3529.2	1	
6	6	3529.9	1	
3	3	3547.5	2	
6	...	3550.8	2	
6	...	3552.8	1	
6	...	3561.1	2	
1	3	3565.7	3	In explosions of O, H with Ni Also a Fe line and in explosions of O, H with [Ni]
2	2	3571.2	3	
2	...	3576.1	3	

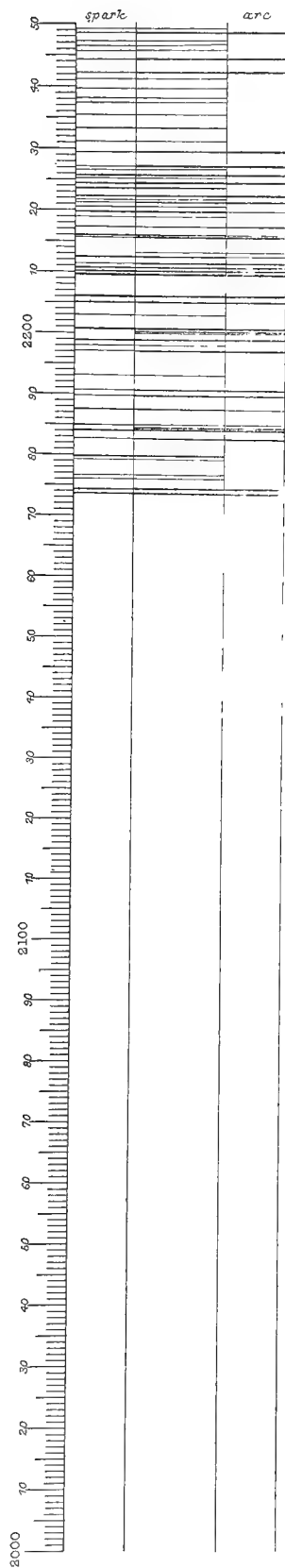
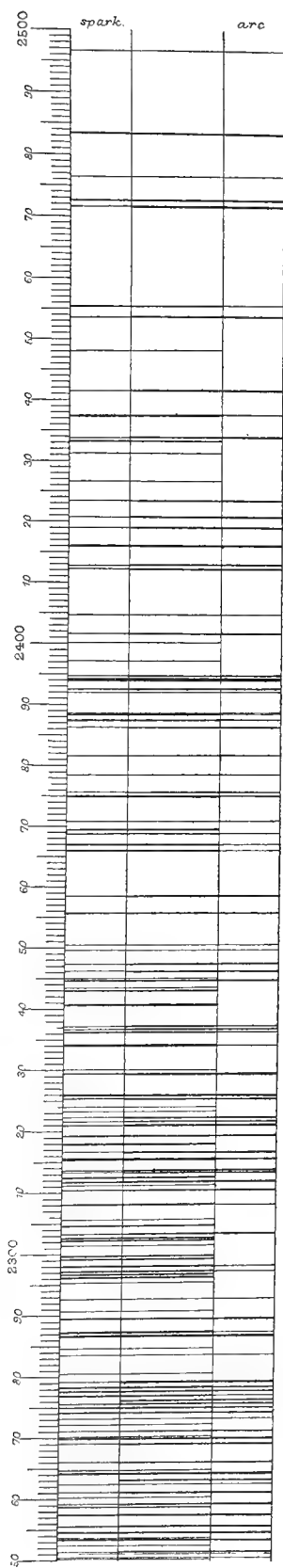
MAP OF THE ULTRA-VIOLET SPECTRUM OF COBALT



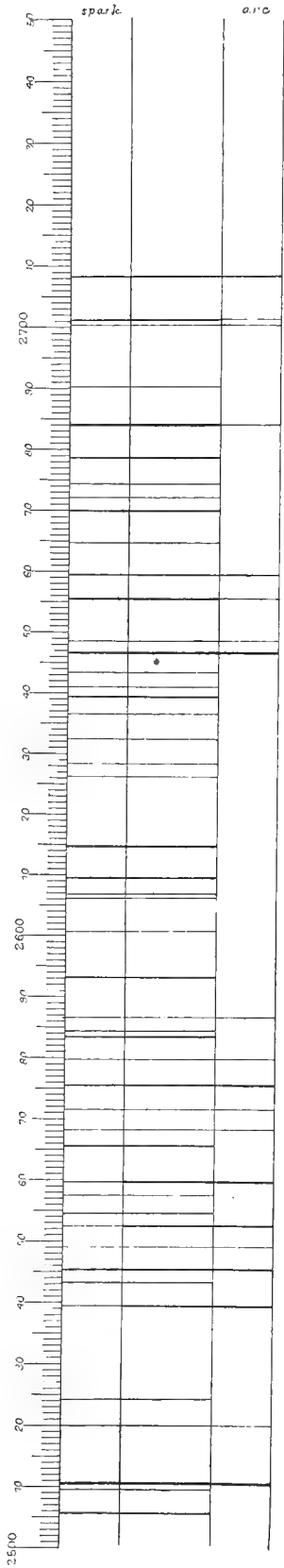
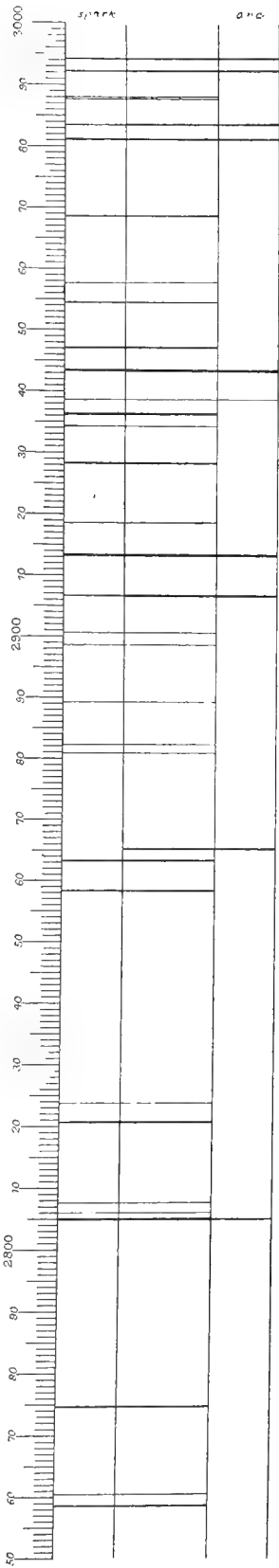
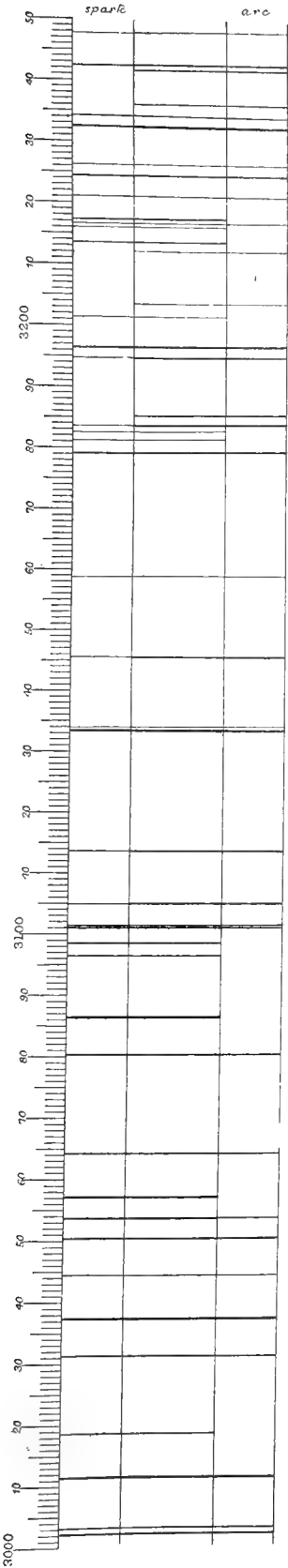
MAP OF THE ULTRA-VIOLET SPECTRUM OF COBALT



MAP OF THE ULTRA-VIOLET SPECTRUM OF NICKEL



MAP OF THE ULTRA-VIOLET SPECTRUM OF NICKEL



MAP OF THE ULTRA-VIOLET SPECTRUM OF NICKEL

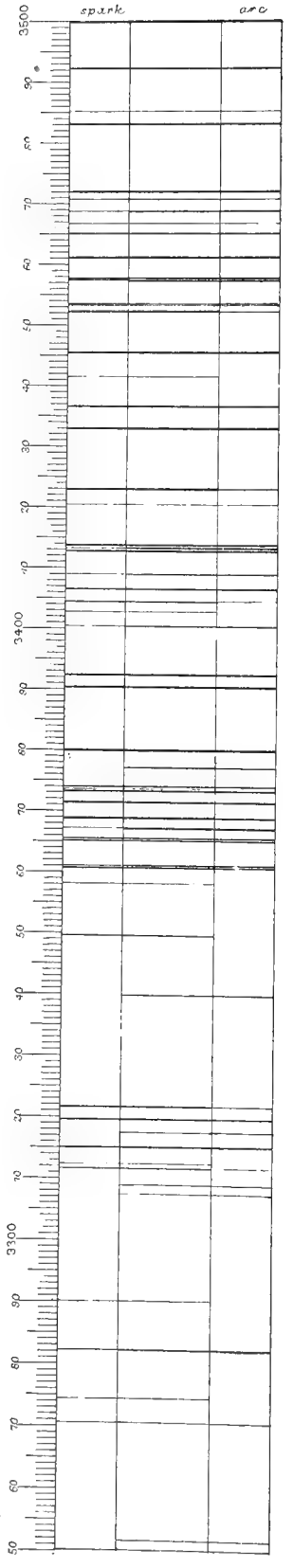
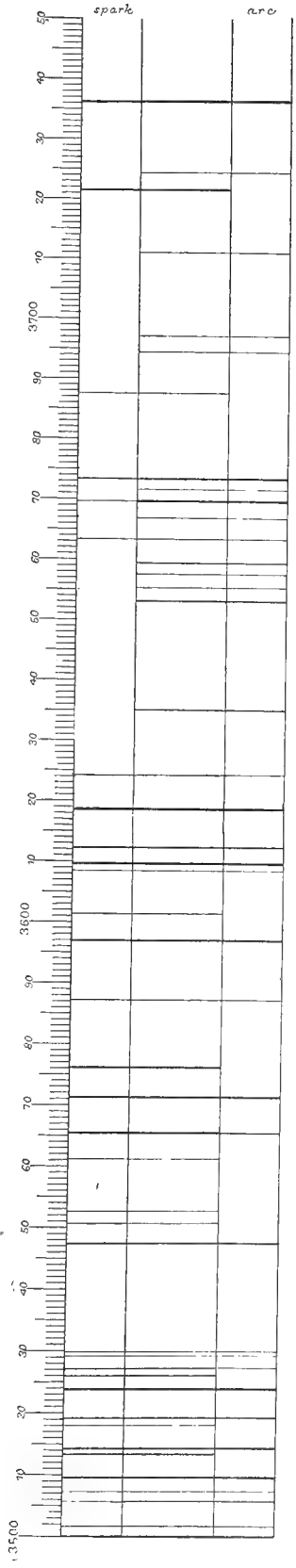
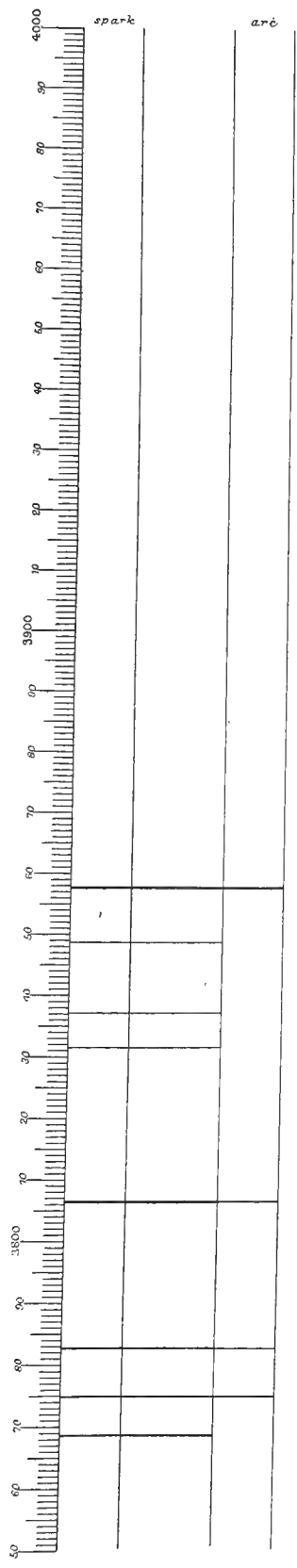


TABLE of Nickel lines—(*continued*).

Intensity		λ		Remarks
Spark	Arc			
5 <i>d</i>	5	3587.2	2	
1	1	3597.0	3	In explosions of O, H with Ni
5	...	3601.4	4	
6	6	3608.6	4	
2	2	3609.8	5	
3	3	3612.1	5	In explosions of O, H with Ni
1	1	3618.8	5	In explosions of O, H with Ni
6	5	3624.1	4	
...	4	3634.9		
...	3	3653.0		
...	6	3655.2		
...	6	3657.5		
...	5	3659.3		
5	...	3663.4	1	
...	6	3666.9		
6	2	3669.7	1	
...	6	3671.5		
5	4	3673.4	1	
6	...	3687.6	1	
...	6	3694.6		
...	6	3697.2		
...	6	3710.9		
3	...	3721.6	1	Also a Fe line
...	6	3724.2		
2	2	3736.1	1	
2	...	3768.9	5	
3	3	3775.0	5	In explosions of O, H with Ni
3	4	3783.0	5	In explosions of O, H with Ni
2	3	3806.6	3	In explosions of O, H with Ni
6	...	3831.7		
5	...	3837.5	2	
5	...	3848.9	2	
2	2	3857.8	7	

NOTE ON THE MAPS OF THE SPECTRA OF COBALT AND NICKEL.

These maps contain many lines which are not in the list in the text. These additional lines were observed in the arc between carbon electrodes when metallic cobalt and nickel respectively were introduced into it; but they were not included in the list in the text because the authors were unable, for the reasons given in the text, to be quite sure that they were not due to other metals contained in the carbon electrodes, or in the crucible in which the arc was taken. It is most probable that the greater part are really due to the metals to which they are assigned in the maps.

The reader is referred to the list in the text for the measured wavelengths, as, owing to a parallactic error in ruling, many of the lines in the maps are placed a fraction of a tenth-meter out of their true places.

INVESTIGATIONS ON THE SPECTRUM OF MAGNESIUM. No. II

[*Proceedings of the Royal Society*, Vol. XLIV. (1888), pp. 241 sqq.]

SINCE our last communication on this subject, we have made many additional observations on the spectrum of magnesium under various circumstances, and have arrived at some new results. Speaking generally, we find that differences of temperature, such as we get in the flame of burning magnesium, in the arc, and in the spark, produce less differences in the spectrum than we had before attributed to them. For instance, the lines which previously we had observed only in the spark discharge, we have since found to be developed in the arc also, provided the discharge occur between electrodes of magnesium*. In making these experiments we used thick electrodes of magnesium, and brought them together inside a glass globe about 6 inches in diameter, fitted with a plate of quartz in front and filled from time to time with various gases. The arc was an instantaneous flash which could not be repeated more than twice without rendering the sides of the vessel opaque with a complete coating of magnesium. It was therefore analogous to an explosion of magnesium vapour. The strong blue line $\lambda 4481$, two pairs about $\lambda 3895$, 3893 , and $\lambda 3855$, 3848 , the strong pair about $\lambda 2935$, 2927 , and the two weaker lines of the quadruple group, namely, $\lambda 2789.9$ and 2797 , all come out in the arc given by a Siemens dynamo between magnesium electrodes in air, in nitrogen, and in hydrogen. We have observed most of them also when the arc is taken in carbonic acid, in ammonia, in steam, in hydrochloric acid, in chlorine, and in oxygen. The relative intensities of these lines, as compared with one another and with the other lines of the spectrum, vary considerably under different circumstances, of which temperature is doubtless one of the most important; but none of the spark lines seem to be absent from the arc, and even the blue line $\lambda 4481$, so characteristic of the spark, which we never found in the electric arc taken between carbon poles in a crucible of magnesia even on addition of magnesium, is sometimes quite as strongly shewn in the arc between magnesium electrodes. There are still several lines of the arc which we have never observed in the spark, such as

* Compare the appearance of the lines of hydrogen in the arc discharge, *supra*, pp. 89, 267.

the series of triplets of wave-length less than 2770, but their presence may be dependent more on the large quantity of incandescent matter in the arc than upon its relative temperature. The observations, however, render doubtful the correctness of the received opinion that the temperature of the spark discharge is much higher than that of the arc. The greater mass of the incandescent matter in the arc may be expected to give a greater number of lines, because the gradations of temperature will be less steep than in a smaller mass, and we shall have from the outer part of the mass the light which is emitted at comparatively low temperatures, while from the inner part we shall get those rays which are only produced by the highest temperatures. Moreover, compounds which may be dissociated in the interior of the mass may be re-formed in the outer part, and produce their characteristic emission or, in some cases, absorption spectra. Heat, however, is not the only form of energy which may give rise to vibrations, and it is probable that the energy of the electric discharge, as well as that due to chemical change, may directly impart to the matter affected vibrations which are more intense than those which the temperature alone would produce.

The Bands of the Oxide.

The set of seven bands in the green, beginning at about $\lambda 5006.4$ and fading towards the violet side of the spectrum, which we have before attributed to the oxide of magnesium, have been subjected to further observation, and we have no reason to doubt the correctness of our former conclusion that they are due either to magnesia or to the chemical action of oxidation. On repeating our experiments with the spark of an induction coil between magnesium electrodes in different gases at atmospheric pressure, we could see no trace of these bands in hydrogen, nitrogen, or ammonia, whether a Leyden jar was used or not. Nor could we see them at all in carbonic oxide, but in this case the brightness of the lines due to the gas might prevent the bands being seen if they were only feebly developed. On the other hand, the bands come out brilliantly when the gas is oxygen or carbonic acid, both with and without the use of a Leyden jar. In air and in steam they are less brilliant, but may be well seen when no jar is used. When a jar is used they are less conspicuous, because in air the lines of nitrogen come out strongly in the same region, and in steam the F line of hydrogen becomes both very bright and much expanded*. It seems, therefore, that it is not the character of the electric discharge, but the nature of the gas, which determines the appearance

* Neither the arc of a Siemens dynamo, nor that of a De Meritens magneto-electric machine, when taken in a crucible of magnesia, shews these bands, even if metallic magnesium be dropped into it. A stream of hydrogen led into the crucible with a view to cool it does not elicit them. When the arc is taken in the open air, and metallic magnesium dropped through it, the bands appear momentarily, but that is probably the result of the burning of the magnesium vapour outside the arc.—May 23.

of the bands; and the absence of the bands in the absence of oxygen, and their increased brilliance in that gas, leave little room for doubt that they are due to the oxide, or to the process of oxidation. It may be assumed that at a sufficiently high temperature magnesia will be decomposed, but magnesia is a very stable compound, a great amount of heat is developed in its formation, and it probably requires a temperature far above that of burning magnesium for its complete dissociation. This is consistent with the appearance of the bands in the spectrum of the flame of the burning metal, as well as in the condensed spark when the other conditions are favourable for the formation of the oxide, or for its stability when formed. In our earlier observations, we obtained in the *visible* region nothing but a continuous spectrum from magnesia heated with the oxy-hydrogen blowpipe; neither the *b* group, nor $\lambda 4570$, nor the triplet near *L* appeared, but at the same time $\lambda 2852$ was not only strong, but was strongly reversed. We now find that this result, so far as it was negative, was a consequence of using too large a mass of magnesia to be adequately heated by the flame. If the piece of magnesia is very small, such as a fragment of the ash of burnt magnesium ribbon, most of the spectrum of burning magnesium is developed in the flame for a short distance from the piece of magnesia. It was not very easy to make these experiments successfully. About 3 inches of magnesium ribbon were burnt in air, and the ash carefully heated in the upper part of the oxy-hydrogen flame to render it dense. The thread of magnesia so obtained was held horizontally with its end projecting into the oxy-hydrogen flame so as to approach the boundary of the inner cone, and if the current of gas were not too strong all that was further necessary was to move up the thread horizontally as the end was worn away. When the magnesia was placed as described, the whole upper part of the flame was of a fine azure-blue colour. Under these circumstances, the flame shews the *b* group and the magnesium-hydrogen series close to it, the bands in the green, the triplet near *L*, the triplet near *M* of the flame of burning magnesium, with the group of bands in that region, and the line $\lambda 2852$. It is remarkable that the proportions in which the oxygen and hydrogen are mixed affect the relative intensities of different parts of the spectrum. In general, both the metallic lines of the *b* group and the bands of the oxide are easily seen; but if the oxygen be in excess the bands of the oxide come out with increased brightness, while the *b* group fades or sometimes becomes invisible. On the other hand, if the hydrogen be in excess the bands fade, and the *b* group shews increased brilliance. There can hardly be much difference in the temperature of the flame according as one gas or the other is in excess, but the excess of oxygen is favourable to the formation and stability of the oxide, while excess of hydrogen facilitates the reduction of magnesium and its maintenance in the metallic state. As regards temperature, it should be observed that while substances merely heated by the flame, and not

undergoing chemical change, are not likely to rise to a temperature above the average temperature of the flame, it will be otherwise with the materials of the flame itself and other substances in it which are undergoing chemical change, and have at the instant of such change the kinetic energy due to the change.

In a recent communication to the Society, "Researches on the Spectra of Meteorites," Mr Lockyer has directly connected the appearance in nebulæ of these bands, namely, "the magnesium fluting at 500," with the temperature of the Bunsen burner (*Roy. Soc. Proc.*, Vol. xliii, p. 133). That the bands are persistent through a large range of temperature there is no doubt, but we cannot help thinking that Mr Lockyer is mistaken in supposing them to be produced at the temperature of a Bunsen burner. It does not follow because the bands are seen when magnesium is burnt in a Bunsen burner that the molecules which emit them are at the temperature of the flame. In the combustion of the magnesium the formation of each molecule of magnesia is attended with a development of kinetic energy which, if it all took the form of heat and were all concentrated in the molecule, must raise its temperature to very nearly the point at which magnesia is completely dissociated. The persistence of the molecule of magnesia when formed will depend upon the dissipation of some of this energy, and one of the forms in which this dissipation occurs is the very radiation which produces the bands. The character of the vibration depends on the motions of the molecules, which in the case in question are not derived from the heat of the flame, but from the stored energy of the separated elements, which becomes kinetic when they combine. The temperature of complete dissociation of magnesia is very far higher than any temperature which can reasonably be assigned to the Bunsen burner.

Nor do the observations we have made on magnesia in the oxy-hydrogen flame appear to us to be inconsistent with the conclusion that the spectrum of the oxide is produced only at a high temperature, as we have a decomposition of magnesia by the hydrogen at the highest temperature of the blowpipe flame, and when hydrogen is in excess little but the metallic lines is visible, because the re-formation of magnesia is, for the most part, the reversal of the former action, and occurs in the cooler part of the flame by the interchange of oxygen between steam and magnesium with scarcely any rise of temperature. On the other hand, when the oxygen is in excess the reduced magnesium carried up into the flame combines for the most part directly with oxygen, and individual molecules thereby acquire a motion of far greater intensity than they could derive from the average heat of the flame.

In fact, when chemical changes are occurring in a flame it cannot be taken for granted that the temperatures of the molecules are all alike, or

that the vibrations which they assume are the result of heat alone. On the other hand, the temperature of the metal separated from magnesia by the oxy-hydrogen flame cannot, we suppose, be at a temperature higher than that of the hottest part of the flame. We are therefore inclined to think that the metallic lines (*b*) are manifested at a lower temperature than the bands of the oxide; and the appearance of a line in the position of the first band without any trace of the second band (which is nearly as bright as the first), and without any trace of the *b* group, is quite sufficient to create a suspicion of mistaken identity when Mr Lockyer ascribes the sharp green line in the spectrum of nebulae to this band of magnesia. This suspicion will be strengthened when it is noticed that the line in question is usually in the nebulae associated with the F line of hydrogen, if it be borne in mind that the spark of magnesium in hydrogen does not give the bands, and that the oxy-hydrogen flame hardly produces them from magnesia when the hydrogen is in excess.

In Mr Lockyer's map of the spectrum of the nebula in Orion (*loc. cit.*, p. 134), he has represented three lines in the position of the edges of the first three of these bands. If these three lines were really seen in the nebula, there would be less room to doubt the identity of the spectra; but the authorities quoted for the map (*loc. cit.*, p. 142) mention only a single line in this position.

When the flame of burning magnesium is viewed with a high dispersion these bands are resolved into series of fine, closely set lines. Seven such series may be counted, beginning at the approximate wave-lengths 5006·4, 4995·6, 4985·4, 4973·6, 4961·6, 4948·6, 4934·4, respectively. When a condensed spark is taken between magnesium electrodes in oxygen mixed with a little air, the pair of strong nitrogen lines may be seen simultaneously with the bands, and lying within the first band, the bright edge of the band being somewhat less refrangible than the less refrangible of the two nitrogen lines.

When the bands are produced by the spark discharge between magnesium electrodes in oxygen or other gas, we have not been able to resolve them into lines, but the whole amount of light from the spark is small compared with that from the flame, and besides it is possible that the several lines forming the shading may be expanded in the spark, and thus obliterate the darker spaces between them.

Triplet near M and adjacent Bands.

Our former account of the spectrum of the flame of burning magnesium included a description of a triplet near the solar line M, and a series of bands extending from it beyond the well-known triplet near L. As we had not observed these features in the spectrum of the spark or arc, and could not trace their connexion with any compound, we concluded that they were

produced by magnesium only at the comparatively low temperature of the flame. We have since found that they are not produced by the metal at that temperature only, but are exhibited as strongly, or even more strongly, in the arc between electrodes of magnesium. In the latter case they appear concurrently with the line at 4481 and other lines which seem to belong to high temperatures. We must therefore regard them as not only produced at the temperature of flames, but as persistent at temperatures very much higher.

The different circumstances under which we have observed this triplet are as follows:—

In the oxy-hydrogen flame when a very small piece of magnesia is held in it. In this case the outer two lines of the triplet are much stronger than the middle line ($\lambda 3724$ about), which in some of our photographs does not shew at all. It should be noticed that the least refrangible of the three lines ($\lambda 3730$ about) is in general more diffuse and not quite so bright as the two more refrangible lines. Magnesia in the oxy-hydrogen flame also gives rise to some bands close to and more refrangible than the triplet, and to another still more refrangible but less bright triplet, in which the lines are set at nearly equal distances from each other, with the approximate wave-lengths 3633·7, 3626·2, 3620·6. These additional bands and triplets are not really absent from the flame spectrum, for traces of them may be seen in some of our photographs of the magnesium flame, but they seem relatively brighter in the oxy-hydrogen flame with magnesia, and the longer exposure of the photographic plate in the latter case helped to bring them out. They seem to come out more strongly under the conditions which make both the green bands of the oxide and the *b* group shew well.

The triplet near *M* is also produced when magnesium oxy-chloride, and when magnesium chloride, is substituted for magnesia in the oxy-hydrogen flame, and in the former case the more refrangible triplet is developed as well.

When carbonic oxide and oxygen are substituted for hydrogen and oxygen, both triplets are developed in the part of the flame near the magnesia, and in this flame the middle line of the triplet near *M* ($\lambda 3724$ about) is as strong as it is in the flame of burning magnesium.

The proper adjustment of the thread of magnesia in this flame is a much more delicate matter than in the oxy-hydrogen flame. In fact, we made many experiments which were failures before we succeeded in getting satisfactory results; and latterly, in order to be certain of success, we had to fill a gas-holder with a mixture of carbonic oxide and half its volume of oxygen and burn the gases as they issued from the holder.

We have not noticed the more refrangible triplet ($\lambda 3633\cdot7$ to $3620\cdot6$ about) under other circumstances, but the triplet near *M* is produced when

magnesia is held in the flame of cyanogen burning in oxygen, in the flash of pyroxylin with which magnesium filings have been mixed, or which has been treated with an alcoholic solution of magnesium chloride.

It is not only very strongly developed, but shews strongly reversed on our photographic plates, in the spectrum of the arc from a Siemens dynamo taken between electrodes of magnesium in oxygen; and most of the accompanying ultra-violet bands of the magnesium flame spectrum are at the same time reversed. It is less strongly, but distinctly, reversed in the spectrum of the same arc taken in air, in carbonic acid gas, and in sulphurous acid gas. It appears also if the arc is taken in ordinary nitrogen unless great precautions are taken to exclude all traces of oxygen or carbonic acid, when it completely disappears. It is developed also in the flash produced when a piece of magnesium ribbon is dissipated in air by the discharge through it of the current from 50 cells of a storage battery. Also in the spark in air at atmospheric pressure between magnesium electrodes connected with the secondary wire of an induction coil when the alternating current of a De Meritens magneto-electric machine is passed through the primary.

In two cases, but only two, we have found this triplet, or what looks like one or both of the more refrangible of its lines, developed in vacuous tubes. In both tubes the gas was air. One had platinum electrodes and a strip of magnesia from burnt magnesium disposed along the tube; the other had fragments of the Dhurmsala meteorite attached to the platinum electrodes. The discharge was that of an induction coil worked in the usual way without a Leyden jar. In each case it is only in one photograph of the spectrum that the lines in question appear. In other photographs taken with the same tubes they do not shew.

On the other hand, this triplet does not make its appearance in the arc from a dynamo between magnesium electrodes in hydrogen, coal gas, cyanogen*, chlorine, hydrochloric acid, or ammonia; nor in the arc from a De Meritens machine in hydrogen or nitrogen. It does not shew in the spark between magnesium electrodes of an induction coil used in the ordinary way, either with or without a Leyden jar, in hydrogen or in air at atmospheric pressure; nor in the glow discharge in vacuous tubes with magnesium electrodes when the residual gas is either air, oxygen, hydrogen, carbonic acid gas, or cyanogen. Nor does it appear, except in the one instance above

* In taking the arc in this way in cyanogen our photographs shew the whole of the five bands of cyanogen between K and L well reversed. We have before noticed (*Roy. Soc. Proc.*, Vol. xxxiii, p. 4, and *supra*, p. 242) the reversal of the more refrangible three of these bands against the bright background of the expanded lines of magnesium when some of that metal was dropped into the arc between carbon electrodes, but in taking the arc between magnesium electrodes in an atmosphere of cyanogen the bright wings of the expanded magnesium lines near L extend beyond the cyanogen bands, and the whole series of the latter are well reversed.—May 23.

mentioned, in the glow discharge in highly rarefied air in a tube containing either magnesia or a strip of metallic magnesium.

A review of all the circumstances under which the triplet near M and its associated bands appear, and of those under which they fail to appear, leads pretty conclusively to the inference that they are due not to merely heated magnesium but to the oxide, or to vibrations set up by the process of oxidation.

With reference to this triplet, Mr Lockyer (*loc. cit.*, p. 122) has referred to us as his authority for the statement that at the temperature of a Bunsen burner as ordinarily employed the ultra-violet line visible is that at 373. We do not agree to this as a statement of observed fact, and we cannot imagine how the passage to which Mr Lockyer refers (*Roy. Soc. Proc.*, Vol. xxxii, p. 202, and *supra*, p. 131, l. 7 from bottom) can be supposed to warrant it. The flame we mention in that passage is not that of a Bunsen burner but that of burning magnesium, which may be very different from the former even when the magnesium is burning in the air which is mixed with coal gas in the Bunsen burner. Moreover, whatever the temperature of the flame may be, we have never observed the triplet at $\lambda 3730$ unaccompanied by other ultra-violet lines. In the flame of burning magnesium, as we state (*supra*, p. 118), "photographs shew, besides, the well-known triplet in the ultra-violet between the solar lines K and L sharply defined, and the line for which Cornu has found the wave-length 2850 very much expanded and strongly reversed."

We have expended a vast amount of time and trouble over vacuous tubes, and our later experiments do but confirm the opinion which we had previously formed that there is an uncertainty about them, their contents and condition, which makes us distrustful of conclusions which depend on them. Photographs of the ultra-violet spectra given by such tubes tell tales of impurities as unexpected as they are difficult to avoid. Every tube of hydrogen which we have examined exhibits the water spectrum more or less, even if metallic sodium has been heated in the tube or the gas dried by prolonged contact with phosphoric oxide. Indeed the only tubes which do not shew the water spectrum have been filled with gases from anhydrous materials contained in a part of the tube itself; and even when tubes have been filled with carbonic acid gas from previously fused sodium carbonate and boracic anhydride the water spectrum is hardly ever absent. The last traces of the ultra-violet bands of nitrogen are almost as difficult to be rid of with certainty. Frequently unknown lines or bands make their appearance, and the same tube will at different times exhibit wholly different spectra. This is especially the case with tubes of rarefied gases which oppose much resistance to the passage of the electric discharge, such as oxygen.

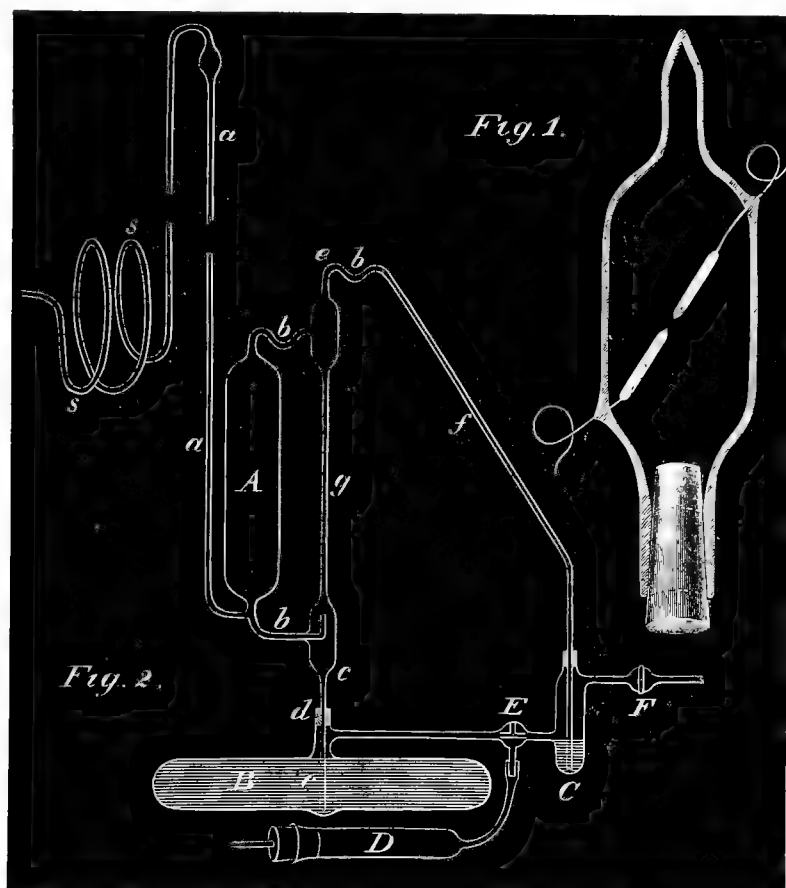
It is no easy matter to prepare tubes for the observation of ultra-violet rays to which glass is opaque. Our plan is to fit a sort of stopper of quartz

to an "end-on" tube (fig. 1). This stopper is a slightly conical piece of rock-crystal with the truncated ends of the cone ground plane and polished. It is first fitted to the tube by grinding and then cemented in with some vitreous substance more fusible than glass. Formerly we employed sodium metaphosphate which answered fairly, but latterly we have used fused silver nitrate which is easier to manipulate. In any case it is very difficult to prevent the tubes cracking under variation of temperature, but if the tube does not crack it is as effectually closed in this way as if it were all of one piece of glass. It is obvious that nitrogen, oxygen, and silver might be derived from silver nitrate used as cement and might add their spectra to those of the other contents of the tube. But the stopper does not lie in the direct course of the discharge, and we have not found that the silver nitrate is in general decomposed. The products of decomposition would at any rate give well-known spectra. The unknown and variable rays we are inclined rather to attribute to substances derived from the glass, either products of decomposition under the action of the electric discharge, or to matters adherent to the surface which become detached under some electric conditions, and adhere again when those conditions are changed. We have photographed the spectrum of one tube which had been filled with oxygen several times and exhausted, and which gave a well-marked spectrum containing a number of rays unknown to us. After a time other photographs of the same tube shewed an entirely different spectrum, and after a further interval the spectrum was found to be again entirely changed, and finally after a further interval the original spectrum reappeared. Changes in the surface tension between the glass and some adherent film may in this case have facilitated the disengagement of the matter of the film and its after re-adherence. Whatever the cause, such changes of the spectra are none the less confusing and suggestive of caution in drawing our inferences from the phenomena of vacuous tubes.

The ultra-violet magnesium lines which we have observed in vacuous tubes with magnesium electrodes, when the induction coil, without jar, is employed, are the triplets at $\lambda 3837$, and the lines $\lambda 2852$, 2802 , and 2795 . These appear whether the residual gas be air, oxygen, hydrogen, or carbonic acid. When a jar is used we have obtained also the triplets at P and S, the pair about $\lambda 2935$ and 2927 , all the quadruple group near $\lambda 2802$ and the quintuple group beyond, and *in one case only*, in oxygen, the group near s , described below, and the flame-triplet near M. When no jar is used sometimes only $\lambda 2852$ is to be seen, sometimes $\lambda 2852$ and the strong pair near $\lambda 2802$, and sometimes also the triplet near L. We infer, therefore, that this is the order of persistency of these lines under the circumstances.

We have before remarked upon the necessity of avoiding all rubber connexions in the construction of pumps employed in the exhaustion of

tubes for spectroscopic observation, and we described a modification of the Sprengel pump which we had constructed for this end (*supra*, p. 104). The warnings of unexpected impurities given by photographs of the ultra-violet spectra of vacuous tubes have shewn the necessity of preventing the contact of the mercury employed with the dust and moisture of the atmosphere. Hence we have used in the experiments described in this paper a mercurial pump constructed wholly of glass, and in which the same mercury



is used over and over again without being exposed to any unfiltered air. For this pump we are indebted to the ingenuity and skill in glass-blowing of Mr Lennox of the Royal Institution. The annexed figure (2) represents its construction. *A* is a reservoir which communicates by the tube *aa*, which ascends vertically some distance in order to prevent any mercury being driven into the exhausted tube, through the spiral tube *ss*, with the tube to be exhausted. *B* is the reservoir of mercury, to the bottom of which the tube *gcc* passes through the sealed joint *d*. The upper part of *B* can be put in

communication through the three-way cock *E*, either with the vessel *C* or with the outer air through the tube *D* which is filled with calcium chloride. *C* forms a mercury valve, and at its upper part communicates through the stopcock *F* with an exhaust pump by which the pressure of the gas in *C* can be quickly reduced to a few millimetres of mercury. When this has been done, the three-way cock *E* is turned so as to cut off the communication between *B* and *C* and open that between *B* and *D*. The pressure of the air filtered through *D* forces the mercury in *B* up the tube *c* until it fills *A* and the whole apparatus, as high as the bend *e*, driving all gas before it through the tube *f* and through the mercury valve *C*, whence it is carried off by the exhaust. The tube *g* is very narrow so as to oppose resistance to the passage of the mercury whereby *A* is filled with mercury as quickly as *g*. As soon as the last bubble of gas has been driven out of *f*, the three-way cock *E* is turned so as to shut the communication with *D* and open that between *B* and *C*. As the pressure of the air on the surface of the mercury in *B* diminishes the mercury falls both in *A* and in *f*, leaving a Torricellian vacuum above it, and, as soon as it has fallen below the end of the tube *a*, the gas in the tube to be exhausted expands into *A*. The same process is then gone through again and again, whereby the whole gaseous contents of *A* are each time removed, and if the volume of *A* be large compared with that of the tube to be exhausted, the pressure of the gas in the latter is very quickly reduced. The bends *bbb* retain a little mercury when *A* is exhausted, and prevent any diffusion from *c* into *A*, and from *f* into *c*. Each time the mercury fills the apparatus a small quantity flows over into *C*, but when it has risen above the opening of the tube connecting *C* and *B*, it passes back into *B*, when the cock *E* is turned so as to open the communication between *C* and *B*.

Group near s.

In their list of lines in the spectrum of magnesium (*Phil. Trans.*, 1884, p. 95) Messrs Hartley and Adeney have given two lines, $\lambda 3071\cdot6$ and $\lambda 3046\cdot0$, which we had not heretofore observed either in the spectrum of the flame, arc, or spark of magnesium; but in our recent observations we have noticed in many cases a well-marked line which, by interpolation between neighbouring iron lines, appears to have a wave-length about $3073\cdot5$, and a pair of narrow bands sharply defined on their less refrangible sides at wave-lengths about $3050\cdot6$ and $3046\cdot7$, and fading away on their more refrangible sides.

We have little doubt that the lines we have observed are identical with those given by Messrs Hartley and Adeney, notwithstanding that there is a much greater discrepancy between the wave-lengths assigned by them and by us than there is between the wave-lengths we have respectively found for the iron lines in the same neighbourhood.

We have noticed the occurrence of this group in the spectrum of the arc from a Siemens dynamo between magnesium electrodes in a variety of gases, in all in fact in which we have examined the arc, except in sulphurous acid gas which is opaque to rays of this refrangibility. Also in the arc from a De Meritens magneto-electric machine between magnesium electrodes in air, in the flash of a magnesium ribbon dissipated by the discharge of a storage battery, in the spark of an induction coil worked in the usual way in air and in hydrogen at atmospheric pressure, and in one instance in the spectrum of an oxygen vacuum tube with magnesium electrodes when a Leyden jar was connected with the secondary wire of the induction coil.

On the other hand, we do not see this group in the spectrum of other vacuum tubes with magnesium electrodes or with magnesia in the tube, nor in the spark from an induction coil in air or hydrogen at atmospheric pressure when the coil is worked with a De Meritens machine on the primary wire, nor in the flame of burning magnesium, nor in the oxy-hydrogen flame with magnesia or magnesium chloride, nor in the arc between carbon electrodes in a crucible of magnesia.

The circumstances under which this group is seen and is not seen, do not seem to indicate that its emission is connected with any particular temperatures so much as with the character of the electric discharge, and perhaps also with the density of the magnesium vapour.

PHOTOGRAPHIC PLATE in illustration of Professors Liveing and Dewar's investigations on the Spectrum of Magnesium, presented by the authors.

Fig. 1 shews part of the spectrum of magnesium burning in air. The strong group in the middle is the triplet near M. The well-known magnesium triplet near L is included in the group of lines to the right of the former.

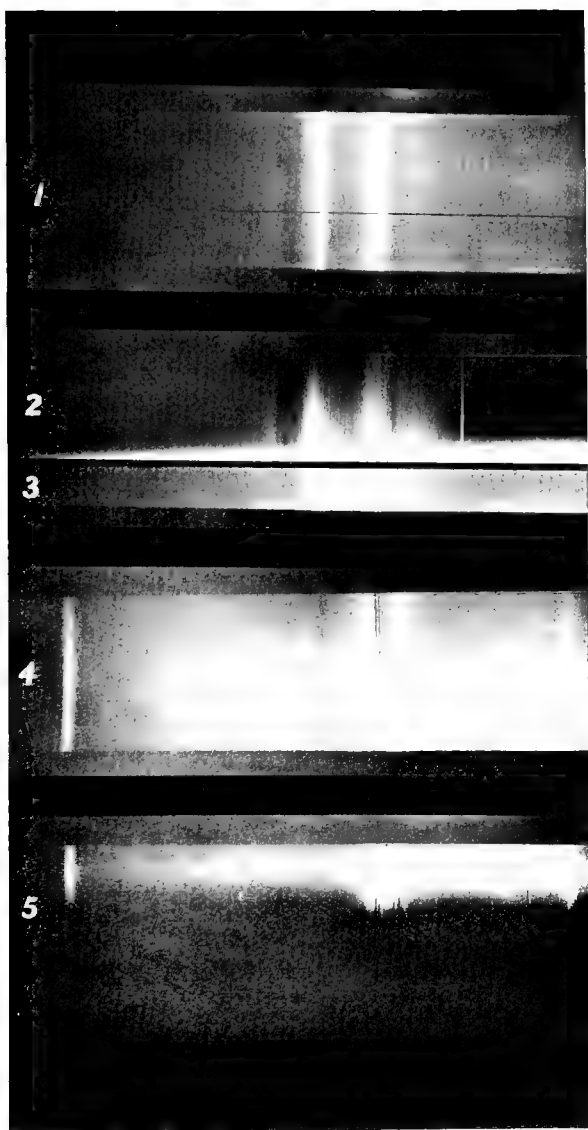
Fig. 2 is the same part of the spectrum of an oxy-hydrogen flame in which a small piece of magnesia was held; the continuous spectrum being due to the solid magnesia.

Fig. 3 is the spectrum of burning magnesium taken without shifting the plate for comparison.

Fig. 4 is the same part of the spectrum of the arc between magnesium electrodes in oxygen. The triplets near M and L are reversed. The group on the left is the triplet near P.

Fig. 5 is the same part of the spectrum of the arc between magnesium electrodes in cyanogen. The magnesium triplet near L is much expanded and self-reversed. The cyanogen bands near it are also reversed.

In all cases the original negatives shew many more details than the print.



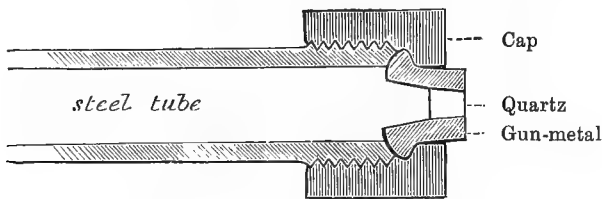
To face p. 376

THE ABSORPTION-SPECTRUM, LUMINOUS AND ULTRA-VIOLET,
OF LARGE MASSES OF OXYGEN

[*Philosophical Magazine*, Ser. 5, Vol. xxvi. (1888), pp. 286 sqq.]

IN the course of experiments on the spectra of gases at high pressures, we have made observations on the absorption-spectrum of oxygen which confirm and extend the observations of Egoroff and Janssen. The interest of this spectrum is so great, on account of the important part which oxygen plays in our world, and its free condition in our atmosphere, and, as we therefore conclude, in the interplanetary space, that it deserves a separate notice.

In order to include the ultra-violet rays in our observations we have had to contrive windows of quartz to the apparatus containing the gases. A strong steel tube, 165 centim. long and 5 centim. wide, was fitted with gun-metal



Section through one end of the tube.

ends, bearing by curved surfaces upon the conical openings of the tube, and forced home by powerful screw-caps. Each gun-metal end was pierced centrally by a conical opening fitted with a quartz stopper, 2.1 centim. thick and of the same diameter, with plane polished ends. A small amount of wax was interposed between the stopper and the gun-metal for the purpose of ensuring a uniform bearing for the quartz, which is very brittle. Trial proved that the tube thus fitted would sustain, without leakage, a pressure of upwards of 260 atmospheres. The tube had, besides, near each end a screw-plug valve for admitting the gases. About the centre of the tube was placed a quartz lens, rather less in diameter than the tube, held in place by three springs which pressed against the walls of the tube. This lens had a focal length of about 46 centim.; so that when a source of light was placed about

10 centim. from one end of the tube, an image of it was formed on the slit of the spectroscope at about the same distance from the other end of the tube, and thereby loss of light, so far as it was due to the distance of the source, was reduced to a minimum.

Ordinary oxygen was let into the tube from an iron bottle until the pressure reached 85 atmospheres, and on viewing an arc light through the tube the following absorptions were visible:—

(1) A very dark band sharply defined on its more refrangible side, gradually fading out on its less refrangible side, and divided into two parts by a streak of light, occupying the position of A of the solar spectrum.

(2) A much weaker but precisely similar band in the position of B of the solar spectrum.

(3) A dark band very diffuse on both edges, extending from about $\lambda 6360$ to $\lambda 6225$, with a maximum intensity at about $\lambda 6305$.

(4) A still darker band a little above D, beginning with a diffuse edge at about $\lambda 5810$, rapidly coming to a maximum intensity at about $\lambda 5785$, and then gradually fading on the more refrangible side, and disappearing at about $\lambda 5675$.

(5) A faint narrow band in the green at about $\lambda 5350$.

(6) A strong band in the blue, diffuse on both sides, extending from about $\lambda 4795$ to $\lambda 4750$.

When photographs were taken of the ultra-violet part of the spectrum of the arc, and of the iron spark, the gas appeared to be quite transparent for violet and ultra-violet rays up to about $\lambda 2745$. From that point the light gradually diminished, and beyond $\lambda 2664$ appeared to be wholly absorbed.

The pressure of the oxygen in the tube was then increased to 140 atmospheres. This had the effect of increasing sensibly the darkness of all the bands above described; but brought out no new bands, except a faint band in the indigo at about $\lambda 4470$. In the ultra-violet the absorption appeared to be complete for all rays beyond about $\lambda 2704$.

The foregoing observations were made with a spectroscope of small dispersion. We next brought to bear on the spectrum a large instrument with one of Rowland's gratings. Even with the high dispersion of this instrument the bands at A could not be resolved into lines; they remained two diffuse bands; though the red potassium-lines, which were produced by sprinkling the electrode of the arc with a potassium-salt, were sharply defined and widely separated. None of the other bands were resolvable into lines. This we attribute to the density of the gas, by which the lines are expanded so as to obliterate the interspaces; and this supposition is confirmed by the observation of Ångström, that the band in the solar spectrum which appears to be identical with that observed by us a little above D was resolved into fine

lines when the sun was high, but appeared as a continuous band when the sun was near the horizon.

On letting down the pressure the bands were all weakened; A, though weaker, became more sharply defined at the more refrangible edge. The faint band in the indigo $\lambda 4470$ remained just visible until the pressure fell below 110 atmospheres. At 90 atmospheres A and B were still well seen and sharp, but all the other bands weaker. B remained visible until the pressure fell to 40 atmospheres. A was then still well seen, the band just above D very faint, and the others almost gone. At 30 atmospheres A was still easily seen, and there was a trace of the band above D. At 25 atmospheres this band had gone, but A remained visible until the pressure fell to less than 20 atmospheres. Hence an amount of oxygen not greater than that contained in a column of air 150 metres long at ordinary pressure is sufficient to produce a visible absorption at A. The quantity of oxygen in the tube at the highest pressure we used falls, however, far short of the quantity traversed by the solar rays in passing through the atmosphere when the sun is vertical.

It will be noted that the bands, if we except the faint two in the green and indigo respectively, appear to be identical with those terrestrial bands in the solar spectrum which Ångström found to be as strong when the air was dried by intense frost as at other times. At least the positions of the maxima agree closely, and that near D shews the same peculiarity in having its maximum near the less refrangible end. We did not, however, observe α , which would be fainter than B, and if, like A and B, unresolvable, would be lost in the diffuse band which covers that region. The bands above numbered 3, 4, 5, 6 agree also with those observed by Olszewski (*Wied. Ann.*, xxxiii, p. 570) to be produced by a layer of liquid oxygen 7 millim. thick. The point also at which the absorption of the ultra-violet rays begins agrees with that at which the absorption by ozone begins, as observed by Hartley (*Journ. Chem. Soc.*, xxxix, p. 57); but the oxygen, as we used it, did not appear to transmit the more refrangible rays beyond 2320 which seem to pass through ozone. Egoroff (*Comptes Rendus*, ci, p. 1144) found that A remained visible when he looked through 80 metres of atmosphere, but 3 kilom. of atmosphere failed to produce α .

When the pressure in our tube was reduced, a cloud was always formed which rendered the contents of the tube nearly opaque; the faint light which was then transmitted had always a green tinge.

It is remarkable that the compounds of oxygen do not shew any similar absorptions. Ångström thought it improbable that oxygen should have a spectrum of such a character, since he failed to obtain an emission spectrum resembling it; and suggested that the absorptions might be due to carbonic acid gas or to ozone, or possibly to oxygen in the state in which it becomes

fluorescent (*Spect. Norm.*, p. 41). Neither carbonic acid gas nor nitrous oxide, at a pressure of 50 atmospheres in our tube, shew any sensible absorption in the visible spectrum; and the absorption of the ultra-violet rays by the latter gas begins at a higher point, namely about $\lambda 2450$, than that of uncombined oxygen. In fact we see the anomalies of the selective absorption by compounds as compared with that of their elements when we take the case of water, which has a remarkable transparency for those ultra-violet rays for which oxygen is opaque.

These observations shew that all stellar spectra observed in our atmosphere, irrespective of the specific ultra-violet radiation of each star, must be limited to wave-lengths not less than $\lambda 2700$, unless we can devise means to eliminate the atmospheric absorption by observations at exceedingly high altitudes.

Postscript.—Since the foregoing paper was written we have extended our observations to much longer columns of oxygen. A steel tube 18 metres long was fitted with the same quartz ends as had been used with the shorter tube, and with two quartz lenses symmetrically placed inside the tube, one near each end, so that when an arc-lamp was placed about 14 centim. from one end of the tube the image of it was formed on the slit of the spectroscope at the same distance from the other end.

When the tube was filled with air only at ordinary pressure no absorptions could be detected, but when the air was replaced by oxygen at the pressure of the atmosphere the absorption of A was just visible, though neither B nor any other absorption-band could be traced. As the pressure of the oxygen was increased A became much darker and more distinct, and B came out sharply defined. The absorption-band about $\lambda 5785$ was next seen, and the dark bands about $\lambda 6300$ and $\lambda 4770$ were just visible when the pressure reached 20 atmospheres.

At a pressure of 30 atmospheres A was very black, B also strong and sharply defined, and the forementioned bands were all quite strong and had the same general characters as when seen through the shorter tube; the band about $\lambda 5350$ also could be seen, but there was only a bare trace of that in the indigo about $\lambda 4470$. At 60 atmospheres these last two absorptions could be well seen, all the other bands were very strong, B still quite sharp, but A somewhat obscured by a general absorption at the red end. At 90 atmospheres this general absorption at the red end seemed to extend to about one-third of the distance between A and B; but A could still be seen, when the slit was wide, as a still darker band on a dark red background; B was still sharp, and the other absorptions all strengthened and somewhat expanded. The diffuse edges of the several bands now extended from about—(1) $\lambda 6410$

to 6190, (2) λ 5865 to 5635, (3) λ 5350 to 5280, (4) λ 4820 to 4710, (5) λ 4480 to 4455.

Photographs taken when the pressure of the oxygen was 90 atmospheres shew a faint absorption-band about L of the solar spectrum, a stronger band extending from about λ 3600 to 3640, a broad diffuse band about the place of the solar line O, and complete absorption above P.

The absorbent column in the tube at the highest pressure used contained a mass of oxygen about equal to that in a vertical column of the earth's atmosphere of the same section as the tube; but the intensity of the bands produced by the compressed gas was far greater than that of the corresponding bands in the solar spectrum with a low sun. When the arc-light was replaced by a piece of white paper reflecting light from the sky through the tube, it appeared to the naked eye to have a faint blue tint, similar to that of liquid oxygen, which, comparing our observation with Olszewski's, seems to have the same absorptive powers as the dense gas, if we except A. This exception is probably only apparent, and due to the difficulty of observing A under the circumstances of Olszewski's experiment.

The greatly increased intensity of the absorption-bands at high pressures bears out Janssen's observation, that in this group the absorption is proportional to the product of the thickness of the absorbent stratum into the square of its density, while the absorptions to which A and B belong vary directly as the density.

The appearance, on looking through the tube when gas at high pressure is streaming into it, is very much like that of a black and a colourless liquid, which do not mix, being stirred together, and the tube soon ceases to transmit any light. Transparency returns as the density becomes uniform. Currents produced by heating the tube at one or two points produce a similar effect, and shew that such currents in the atmosphere of a star may stop all rays coming from its interior.

We hope before long to get the tube fitted with rock-salt ends and lenses, and to determine the total absorption of radiation by similar masses of oxygen, nitrogen, and hydrogen.

NOTES ON THE ABSORPTION-SPECTRA OF OXYGEN AND
SOME OF ITS COMPOUNDS

[*Proceedings of the Royal Society*, Vol. XLVI. (1889), pp. 222 sqq.]

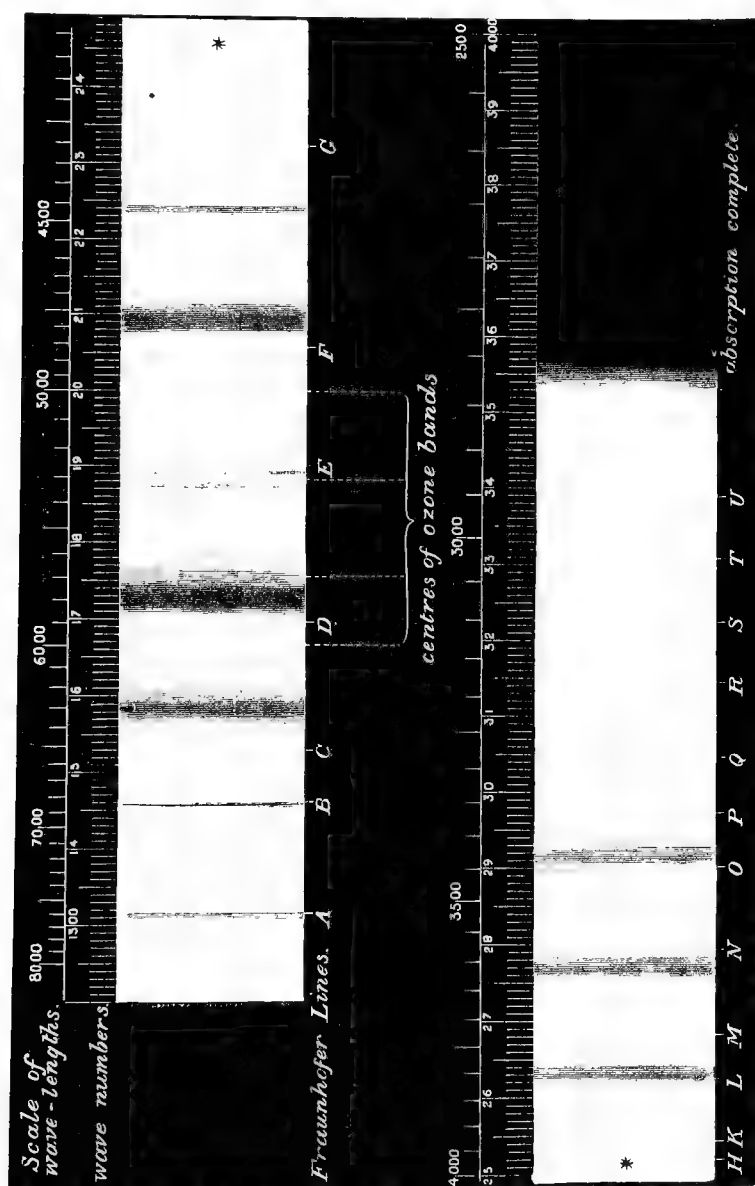
THE absorption-spectrum of oxygen has engaged attention not only on account of the important part which that element plays in the world, but because of the remarkable character of that absorption, so strongly marked, exhibiting bands of two essentially different classes, and extremely variable under varying circumstances of condensation and combination.

It may be expected that the study of it will reveal something new as to the nature of the molecular changes brought about by different circumstances, physical and chemical.

We have already published notes of some of our experiments on this subject (*supra*, p. 377), and these confirm generally the observations of Egoroff, Janssen, and Olszewski.

The accompanying diagram represents the absorption of 18 metres of ordinary oxygen gas at a pressure of about 97 atmospheres, that is, of a mass of oxygen rather greater than is contained in a vertical column of equal section of the earth's atmosphere. Under the circumstances of the experiment the absorptions A and B are very black, and the lines of which they are composed appear much broader than in the ordinary solar spectrum. The other bands are all diffuse at their edges, and, so far as we have observed, unresolvable into lines. It will be noted that the complete absorption of the ultra-violet rays does not extend quite so far down as the limit of the solar spectrum, though it approaches that limit. There is a diffuse edge of gradually diminishing absorption succeeding the complete absorption, and this fact, together with the rapid diminution of the extent of the complete absorption with decrease of pressure, lead us to class this absorption of the extreme rays with the diffuse bands, which, according to Janssen, increase in intensity as the square of the density of the gas. If that be so, it is unlikely that the limit of the solar spectrum is due to the absorption of ordinary oxygen. For though we may suppose interplanetary space to be pervaded by materials similar to our atmosphere, yet they must be in such a state of

tenuity that, although they may to some extent reinforce A and B, they will not add sensibly to the strength of the diffuse bands. Moreover, these bands, though identical in position, so far as the blue or less refrangible part of the



spectrum is concerned, with bands observed by Brewster and others in the solar spectrum, are seen much more strongly through our tubes of compressed oxygen than they appear in the solar spectrum with a low sun. The ultra-violet bands, of which the one near N appears in our photographs nearly as

strong as the band just above F, and that in the indigo, have not, so far as we are aware, been noticed in the solar spectrum. Probably they would appear if photographs were taken with small dispersion when the sun was low.

As the pressure in the tube diminished, the bands rapidly faded; that in the indigo, with an oscillation-frequency or wave-number about 2240, was the first to disappear, then those near L and O and that near E. At the same time the limit of the transmitted ultra-violet light advanced from an oscillation-frequency of about 3575 at 97 atmospheres, to 3710 at 50 atmospheres and 3848 at 23 atmospheres. At 20 atmospheres the three bands above C, D, and F, respectively, were still visible, though faint. B remained visible until the pressure was reduced to 2 atmospheres, and A could still be seen, but with difficulty, when the pressure of the 18 metres of oxygen was reduced to 1 atmosphere.

When atmospheric air was substituted for oxygen we found that 7 atmospheres was the limit of pressure at which we could certainly distinguish A, and 18 atmospheres the limit at which we could see B. It is a difficult matter to say exactly when an absorption becomes invisible, but the observations on air were made under the same circumstances as those on oxygen, and the two sets of observations were fairly comparable. With air at 75 atmospheres the three bands above C, D, and F, respectively, could all be seen, but that near C only with difficulty. The mass of oxygen and its *partial* pressure in the tube was in this case less by about one-quarter than that which was required to bring out the bands when oxygen alone was used. The cause of this may be that the development of the diffuse bands depends in some degree on the total pressure of the air, and not only on the partial pressure of oxygen in it.

The mass of oxygen which when unmixed with nitrogen made A visible would correspond to that in the tube filled with air at 5 atmospheres, and that which made B visible would correspond to air at 10 atmospheres. The differences between these pressures and those which are actually needed to render A and B visible seem too great to be ascribed to errors of observation, and seem to indicate that the addition of the nitrogen has some effect on the absorptive action of the oxygen. On the other hand, Egoroff found that he could still distinguish A when the thickness of air at ordinary pressure was reduced to 80 metres (*Compt. Rend.*, Vol. ci, p. 1144). This amount of air corresponds to rather less oxygen than our tube would hold at a pressure of 1 atmosphere. Differences in the sources of light, in the spectroscope, and the observers, would, however, count for a good deal in observations of this kind.

In order to try the influence of temperature on the absorption, the shorter of our experimental tubes, 165 cm. long, was surrounded by a jacket filled with a mixture of solid carbonic anhydride and ether, which was rapidly

evaporated by means of a large air-pump. By this means the temperature would be reduced to -100° . The absorption of oxygen at several different pressures up to 104 atmospheres was observed through the cooled tube. We were not, however, able to detect any increase of intensity, or other change, in the absorptions which could be ascribed to the cooling. To try the effect of an increase of temperature, the 18-metre tube was surrounded by a jacket and heated up to 100° by steam. Heating appeared to render the diffuse bands rather more diffuse and less distinct. On the whole the influence of a change of temperature of 100° either way is slight.

We have observed repeatedly the absorption of liquid oxygen in thicknesses of 8 and 12 mm. Our observations confirm those of Olszewski. 8 mm. of liquid oxygen gives plainly the three diffuse bands above C, D, and F, respectively. With a thickness of 12 mm. we were not able to detect any more.

We observed the absorption produced by liquid oxygen on the one hand when it was cooled by its own evaporation until the tension of its vapour was only equal to that of the atmosphere, that is, to a temperature of -181° according to Olszewski, and also when the temperature of the liquid was allowed to rise under pressure up to nearly the critical temperature. There appeared to be no appreciable difference in the absorption under these different circumstances when the oxygen was completely liquid, when it was near its critical temperature, and when it was completely gaseous; so far at least as concerns the three principal bands, which were all that could be seen in the light transmitted by the liquid in a thickness of 12 mm.

It will be observed that taking the density of oxygen at -181.4° to be 1.124, as given by Olszewski, 12 mm. of the liquid would be equivalent to 9.37 metres of the gas at atmospheric pressure—hardly more than half the thickness required to make A visible. The experiments, therefore, point to the conclusion that gaseous and liquid oxygen have the same absorption-spectrum. This is a very noteworthy conclusion. For, considering that no compound of oxygen, so far as is known, gives the absorptions of oxygen, the persistency of the absorptions of oxygen through the stages of condensation to the state of complete liquidity implies a persistency of molecular constitution which we should hardly have expected.

In order to compare the absorption of ozone with that of oxygen we employed a tube 12 feet long, made of tinplate fitted with glass ends and coated with paraffin on the inside. We could not use the 18 m. steel tube on account of the action of the ozone on the metal which rapidly reduced the proportion of ozone, and also because we could not conveniently cool it. Ozonised oxygen was passed into the tin tube for some time, while the ozoniser and the tube itself were cooled with ice and salt. The lime-light, viewed through the tube, looked very blue, and also the spot of light thrown

through the tube on to a sheet of white paper was equally blue, indicating a considerable absorption of the less refrangible part of the spectrum. The absorption, so far as the visible rays are concerned, appeared to be of a general character, for the spectroscope revealed only four extremely faint absorption-bands. The centres of these bands were at about the wave-numbers 1662, 1752, 1880, and 1990, and their positions with reference to the bands of oxygen are indicated in the diagram. They were so faint as to be seen only with difficulty. When the hot carbon of an arc lamp was substituted for the lime-light they were rather more distinct, but the positions of the edges were undefinable. The light of a gas-lamp was insufficient to shew them, and they were no better seen with a single-prism spectroscope of low dispersive power than with the spectroscope we employed for observing the oxygen. Only one of these bands, it will be seen from the diagram, is nearly coincident with an oxygen-band, namely, that near E, the faintest of the oxygen-bands. That at wave-number 1752 overlaps the strongest oxygen-band, but not at its strongest part, and has none of the peculiar character of its shading, abruptly increasing on the less refrangible side and slowly decreasing on the other side. Photographs of the spectrum (taken through a tube with quartz ends) shewed that the ozone absorbed all the rays above the wave-number 3086—a point between Q and R—while partial absorption extended below Q. We may say, therefore, that we can trace no identity between the absorptions of ozone and those of ordinary oxygen. There is no mere displacement of the bands, such as we sometimes get when a coloured substance is dissolved in different menstrua, nor any such a resemblance as we have between the absorption-bands of the different cobaltous salts derived from different acids.

The four bands which we see to be produced by ozonised oxygen correspond fairly with the 2nd, 3rd, 5th, and 6th of the bands described by Chappuis as due to ozone (*Annales de l'École Normale*, 2nd ser., Vol. xi, May, 1882). These four bands, he says, are the first to be seen. We have failed to perceive any others with the 3·66 m. tube, though the oxygen was highly ozonised and maintained at a low temperature. None of the bands were of sufficient intensity to make themselves visible on our photographic plates.

It will be noted that the absorption by ozone extends far below the limit of the solar spectrum. We found, however, that by diminishing the proportion of ozone to oxygen in the tube the limit of the transmitted light was continually advanced, as already described by Hartley. The limit of the solar spectrum may, therefore, very well be determined by the average amount of ozone in the atmosphere, as Hartley supposes. The known variations in the limit of the solar spectrum may be taken as confirmatory of this hypothesis, although the comparatively small amount of those variations is certainly less than we should have expected if they measure the changes in the proportion of ozone in the atmosphere.

The absorptions of the class to which A and B belong must be those which are most easily assumed by the diatomic molecules (O^2) of ordinary oxygen. Whether oxygen in more complex molecules, as in ozone (O^3), may be capable of taking up the corresponding vibrations cannot easily be determined because we cannot isolate ozone; but since none of the compounds of oxygen with nitrogen, hydrogen or carbon, or, so far as known, with any other element, exhibit these absorptions, it is very probable that they are peculiar to the molecule O^2 . From this point of view it will be interesting to determine—as we hope to do shortly—whether liquefied oxygen, which we suppose to have more complex molecules, produces these absorptions. The corresponding spectrum of emission has not as yet been observed, probably because the agency employed to render the gas luminous breaks up the molecules into single atoms of oxygen.

As for the other class of absorption, the diffuse bands, since they appear to have intensities proportional to the square of the density of the gas, they must depend on a change produced by compression. This may either be the formation of more complex molecules, as for example O^4 , corresponding to the deviation from Boyle's law exhibited by oxygen gas, or it may be the constraint to which the molecules are subject during their encounters with one another. Increase of temperature would affect the former, tending to diminish the number of complex molecules formed at a given pressure, but would have no effect on the latter, for though the number of encounters of the molecules in a given interval of time would be greater the higher the temperature, yet so long as the volume was unaltered the ratio of the duration of an encounter to that of free motion would be sensibly unaltered. So far as any change due to temperature has been observed, it is that a rise of temperature slightly weakens the diffuse absorptions.

Reverting to the compounds of oxygen, none of them shew the absorptions of oxygen, not even the general absorption of the ultra-violet rays. Some of them, such as water and carbon dioxide, appear quite transparent to ultra-violet rays, while in others, such as nitrous oxide, which shew a general absorption of the ultra-violet rays, the limit of transparency is different from that of oxygen. In other respects we may say that there is no resemblance between the absorptions of the compounds of oxygen and those due to oxygen itself. Some of the former have very definite and characteristic absorptions, such as the well-known spectra of the peroxides of nitrogen and chlorine, and we must regard these as indicating the rates of vibration which the molecules NO^2 and ClO^2 respectively are capable of easily taking up. The absence of the absorptions due to oxygen from all compounds of oxygen seems to indicate either that chemical combination is not, as has been supposed by some chemists, a temporary relation in which the molecular groupings are continually breaking up, to be formed anew with ever-changing elementary

atoms; or, that the periods of dissociation are very small compared with the periods of association. For otherwise we should expect that such compounds of oxygen as CO^2 and NO^2 must always have amongst their molecules some molecules identical with those of oxygen and capable of taking up vibrations of the same period. At least we must conclude that little, if any, of the oxygen of these and other compounds is ever out of the influence of the other components.

We have re-examined the absorption-spectrum of N^2O^4 at various temperatures, and agree to the conclusion of Bell (*Amer. Chem. Journ.*, Vol. vii, p. 32) that N^2O^4 , whether liquid or gaseous, effects only a general absorption at either end of the spectrum, and that the selective absorptions observed with it are due to the presence of NO^2 .

In order to obtain pure N^2O^4 , the tube in which the liquid was sealed was placed in a freezing mixture, and a large part of the liquid frozen; the remaining liquid was then drained as completely as possible into the other end of the tube, and sealed off.

It should be observed that the crystals of N^2O^4 appear colourless, and that when they are melted the liquid and superincumbent vapour are of a very pale yellow colour. As the temperature rises both liquid and vapour become, as is well known, of a deep orange, and finally of a dark, reddish-brown colour. We examined the spectra produced by two thicknesses of liquid and vapour—(1) by that contained in a narrow tube about 1 mm. in diameter, and (2) by that in a tube about 1 cm. in diameter. At 15° to 20° the vapour in the narrow as well as in the wider tube shewed the well-known absorption-spectrum of fine, dark lines; no absorption by the liquid in the narrow tube could be detected, and the liquid in the wide tube shewed no fine lines, but several faint, very diffuse bands, unresolvable into lines with a spectroscope of three prisms. These bands had their maxima in places where the fine lines of the vapour were most intense and most closely set, so that it might be inferred that they were due to similar molecules in both cases, but that in the liquid the vibrations of these molecules were no longer sharply defined but modified by the constraint arising from the liquid state. Some parts, however, of the spectrum of the vapour, where the lines were closely set, did not appear to be represented by any definite bands in the liquid. The liquid absorbed a good deal of blue light in a continuous manner, while the vapour only absorbed it selectively. At the red end the limit of the visible spectrum was lower for the liquid than for the gas, that is, there was more absorption of red light by the vapour than by the liquid, so much so that below a certain point the absorption by the vapour appeared continuous.

The narrow tube was next immersed in a wider tube full of glycerine, which was gradually heated. As the temperature rose, the colour of both

liquid and vapour deepened, the absorptions of the vapour were stronger, and the liquid gave the same bands as had been before observed with the greater thickness. At still higher temperature the absorption of blue light, both by liquid and vapour, diminished sensibly, until at 85° the groups of lines in the blue had pretty well disappeared from the spectrum of the vapour. In fact, at 85° there was no sensible difference between the actions of liquid and vapour on blue light, it seemed only some continuous absorption. At the red end the difference between the liquid and vapour remained quite as strongly marked as at lower temperatures, if anything, more so; and the absorptions in the orange, yellow, and green were unaltered. At 90° the lines of the vapour in the green began to fade, and at 100° they were very faint; but those in the orange, as well as the corresponding diffuse bands in the liquid, were as strong as before. There was still considerably more absorption of red light by the vapour than by the liquid, as if the vapour gave, in the red, a strong absorption-band which was not given by the liquid.

As the temperature rose to 110° all the lines in the vapour had become faint, and at 115° they were no longer discernible, and there was no difference between the spectra of liquid and vapour except in the red, and even here the difference was less marked than at lower temperatures. At 130° no distinction was observable between the spectra of liquid and vapour, there were no lines or bands in either, but a good deal of general absorption. Liquid and vapour were dark, and appeared much of a colour, but the meniscus at the junction was quite evident. The tube was further heated to 155° , but no further change was noticed in the spectrum. On gradually cooling the tube, at 112° the least refrangible band in the orange was seen coming in both in vapour and liquid, diffuse in both. At 100° the usual lines were well seen in the orange, yellow, and citron of the vapour, faint lines in the green, and none in the blue; and subsequently the appearances presented on heating followed in the reverse order.

A solution of N^2O^4 in carbon bisulphide gave, in a thickness of 7 or 8 cm., diffuse absorption-bands in the green and citron, ill-defined as in liquid N^2O^4 , and in corresponding positions. In a thickness of 1 cm. these bands were no longer visible.

These observations bear out the supposition that pure N^2O^4 is without selective absorption of the visible rays, and that the absorption observed is due to NO^2 , both in the vapour and liquid, this absorption being modified in the liquid by the state of solution in which the molecules have much less freedom. As the temperature rises the proportion of NO^2 increases, and at the same time the density of the vapour increases and the freedom of motion of the molecules is diminished, they are less able to assume the more rapid vibrations, and those which they do assume become less sharply defined, so that the lines fade into bands and ultimately into a general absorption.

Taking Willard Gibbs's expression ("Equilibrium of heterogeneous substances," *Connecticut Acad. Trans.*, Vol. iii, p. 239) for the density D , in terms of the pressure in atmospheres p , at temperature t°

$$D = 3.178 + \theta - \sqrt{\theta(3.178 + \theta)},$$

where
$$\log_{10} \theta = 9.47056 - \frac{3118.6}{t + 273} - \log_{10} p,$$

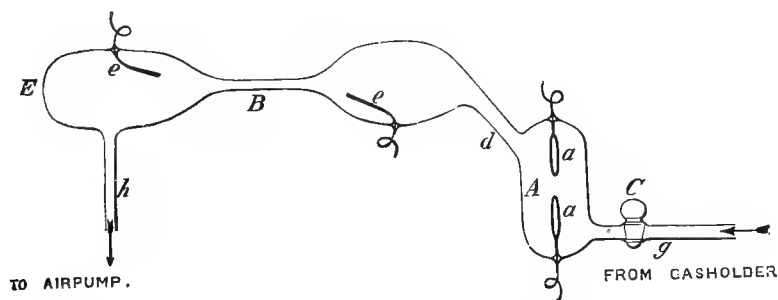
as deduced from Deville and Troost's experiments, we find the density of NO_2 at 140° and 50 atmospheres, equal to 2, *i.e.*, equal to the density of N_2O_4 vapour at 60° and 1 atmosphere.

Dewar and Ansdell found the critical temperature for N_2O_4 to be 156° .

THE SPECTROSCOPIC PROPERTIES OF DUST

[*Proceedings of the Royal Society*, Vol. XLVIII. (1890), pp. 437 sqq.]

THE suggestion that the auroral spectrum, the principal ray in the spectrum of nebulae, and other rays of unknown origin, might be due to meteoric dust induced us to investigate the problem whether solid particles of sufficient minuteness would act like gaseous molecules in an electric discharge and become luminous with their characteristic special radiation. The dust we employed was that thrown off from the surface of various electrodes by a disruptive discharge, and it was carried forward into the tube of observation by a more or less rapid current of air or other gas. The arrangement will be best understood from the annexed diagram, which represents a section



of the glass vessel which was the principal part of the apparatus. *A* represents a bulb, in which were the electrodes *a, a* to give the dust, connected by a wide tube *d* with the tube for observation *B*. The end *E* was blown clear, so that the narrow part of *B* could be observed end-on. The electrodes *e, e* were of platinum. The tube *g*, passing from *A* to the supply of gas, was fitted with a glass stopcock *C* for regulating the intake, and the tube *h* led from the distant end of *B* to the air-pump. The air-pump was a large one worked by a gas-engine capable of keeping the pressure down to a few millimetres, even with a considerable leakage. Observations were made of the discharge in *B*

at various low pressures, sometimes with, and at other times without, a Leyden jar in circuit. The sparks in *A* were generally taken with a jar, and there was ample proof, if proof were needed, of the dust derived from the electrodes, since it formed a visible deposit in the tube *d*, in the first bulb of *B*, and even on the end *E*. The air or other gas passed into *A* was filtered through cotton-wool to remove all dust before admission to the apparatus.

Various metals were used as electrodes in *A*, magnesium, iron, manganese, cadmium, fused calcium chloride, metallic sodium in a little glass cup on a platinum wire, and fragments of the Dhurmsala meteorite; but in no case could the rays of any of the substances employed be seen in the discharge through *B*, either when a Leyden jar was in circuit or not.

Incidentally, we found that magnesium electrodes were not so good as some of the other metals for these experiments, because the apparatus was never wholly free from traces of air, and lines or bright edges of bands of nitrogen fall very near the most characteristic lines of magnesium, and with small dispersion might easily be mistaken for them.

Air, hydrogen, carbon dioxide, and oxygen, were successively used as the gases passing through the apparatus, and at various pressures from 2 mm. up to 20, and, in some cases, up to 40 mm., but with the same result; no rays, due to the electrodes in *A*, could be detected in *B*. Even when one of the electrodes in *A* was sodium, and the sodium rays, orange, yellow, citron, green, and blue, were brilliant in the spectrum of *A*, not even the D lines could be detected in *B*. We should have expected that some traces of sodium *in the state of vapour* would have been carried by the stream of hydrogen into *B*; but it seems that it was not so; nor could the apparent absence of rays due to the dust, be ascribed to mere faintness in their light, for we took photographs of the spectrum of *B*, and found that even lengthened exposures produced no evidence of rays due to the dust; nor could it be ascribed to the character of the discharge in *B*, for the discharge was varied; sometimes *A* and *B* were in the same circuit; sometimes the discharge in *B* was from a separate coil, and even the powerful discharge from a large coil stimulated by a De Meritens magneto-electric machine, was tried.

That abundance of dust was formed by the sparking in *A* was proved not only by the deposit in the tube, but by allowing the stream of gas at atmospheric pressure from the tube *h* (of course disconnected from the pump) to impinge on a flame, when the characteristic flame-spectrum of the electrodes in *A* was at once manifest. When the gas used was hydrogen, and it was burnt in oxygen, the spectrum of the electrodes was particularly well seen; also when the gas was oxygen and led into a hydrogen flame.

That the dust was of extreme fineness and capable of being carried by

a stream of gas to a great distance was proved as follows:—a stream of hydrogen, at ordinary pressure, was passed through the sparking tube with magnesium electrodes, and then through more than 100 feet of metal tube in a coil, and, finally, burnt as it issued. Before the sparking began there were no signs of magnesium in the flame; but when sparks had been passing between the magnesium electrodes for a short time, the magnesium spectrum was seen in the flame. It took 55 seconds for the gas to carry the dust through the long pipe, and when the sparking ceased it was again about the same time before the magnesium disappeared from the flame. It always appeared and disappeared sharply in correspondence with the sparking. Similar experiments, but with a shorter tube, were made with other metals, iron, sodium, lithium, &c., always with like results; also a current of oxygen was passed through the sparking tube and into a flame of hydrogen, and produced similar effects. Even aluminium, which does not usually shew any part of its spectrum when used as an electrode in a vacuous tube, gave, when sparked in oxygen, dust which, when carried into a hydrogen flame, shewed the characteristic bands of alumina.

Considering that a sensible amount of dust was deposited in the bulbs of *B*, we should have expected that some would be deposited on the electrodes *e*, *e* in that tube, and that the discharge from electrodes so coated would give the spectrum of the metal on their surface. There is no doubt that when no discharge was taking place in *B* the electrodes *e*, *e* did receive their share of dust; and, if it had been allowed to accumulate so as to form a coherent crust, it would have given its characteristic spectrum on first passing sparks in *B*. But, so long as the dust is loose, the passage of a discharge instantly clears the electrodes of all dust, and seems to dispel all dust from the gas through which the discharge occurs. It is well known that an electric discharge in a vessel of air has the effect of clearing out of the air all the particles that serve as nuclei for the condensation of water; and we made several experiments with a view to determine whether a similar effect was produced on the dust in our tubes. The gas from the sparking tube was carried through a glass globe, and so on to the jet where it was burned; a wire connected with one pole of a Voss or Wimshurst electric machine projected into the interior of the globe, and a patch of tinfoil on the outside of the globe was connected with the other pole of the electric machine. So long as the Voss machine was not worked, the gas carried the dust from the sparking tube through the globe, and it was seen in the spectrum of the flame, or simply in the colour of the flame when lithium was one of the electrodes; but, on working the machine so as to produce a silent discharge inside the globe, the flame, in one or two seconds, suddenly ceased to shew the spectrum of the dust, and in the case of the lithium lost its red colour. When the machine was no longer worked, the spectrum or colour speedily reappeared, to vanish again suddenly when the machine was started afresh. When a narrow tube,

with a piece of tinfoil outside and a wire inside, was substituted for the globe, the like results ensued.

It appears, then, not only that dust, however fine, suspended in a gas will not act like gaseous matter in becoming luminous with its characteristic spectrum in an electric discharge, but that it is driven with extraordinary rapidity out of the course of the discharge. If, then, the spectrum of the aurora be due, not to the ordinary constituents of our atmosphere, but to adventitious matter from planetary space, we conclude that such matter must be in, or must be brought into, the gaseous state, or at least have its properties entirely altered from those it possesses at ordinary temperatures, before it becomes luminous in the electric discharge.

ON THE INFLUENCE OF PRESSURE ON THE
SPECTRA OF FLAMES

[*Proceedings of the Royal Society*, Vol. XLIX. (1891), pp. 217 sqq.]

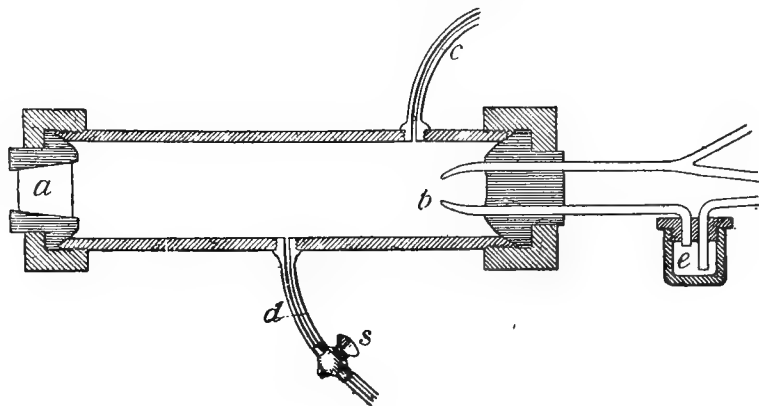
WE have already described (*supra*, p. 322) the remarkable spectrum of the oxy-hydrogen flame burning at the ordinary atmospheric pressure. Recently we have examined the spectrum of the same flame at various pressures: hydrogen burning in excess of oxygen up to a pressure of 40 atmospheres, and oxygen in excess of hydrogen up to a pressure of 25 atmospheres, also that of the mixed gases burning in carbonic acid gas.

The apparatus employed was an adaptation of one of the tubes used in our experiments on the absorption spectra of compressed gases (*supra*, p. 377). It consisted of a steel cylinder, about 50 mm. in internal diameter and 225 mm. long, fitted at one end with a quartz stopper, *a*, in the figure overleaf, and with a jet, *b*, for burning the gas, adapted by a properly fitting union joint to the opposite end. There were two tubes, *c* and *d*, connected to the cylinder at the sides, of which one, *c*, served for the introduction of gas, while the other, *d*, was fitted with a stopcock and was used to draw off the water formed, or to reduce the pressure of the gas in the cylinder if that was desired. The flame was observed, nearly end on, through the quartz stopper. The whole apparatus was kept cool by a stream of cold water running on to a sponge cloth wrapped round the cylinder. In the course of the tube conveying gas to the jet *b* was interposed a small cylinder, *e*, in which sodium was placed, and by heating this, the gas entering could be charged with sodium vapour.

The gases were supplied from steel cylinders into which they had been compressed, and the pressure was registered by a gauge attached to the tube by which the gas entered the experimental cylinder. Commercial compressed gases were used, containing a sensible percentage of air.

When hydrogen was the gas forming the burning jet, it was lighted at the end of the tube *b* before introducing it into the experimental cylinder. When it was desired to have a jet of oxygen burning in hydrogen, this could be managed by introducing oxygen through the second tube and increasing the

supply of hydrogen until the flame passed over to the oxygen jet. The same result was sometimes attained by first filling the experimental cylinder by a gentle stream of hydrogen through the side tube *c* before the end with the tube *b* was screwed on; the hydrogen as it issued was then lighted, and the jet, with a gentle stream of oxygen issuing, inserted and screwed down. The stopcock *s* was kept open until this was done, and then by closing *s*, and admitting more gas from the reservoirs, the pressure in the experimental cylinder could be increased at pleasure.



Hydrogen Burning in Oxygen.

The first observations were made with a jet of hydrogen burning in oxygen. As the pressure rose, the luminosity of the flame increased, as long ago described by Frankland (*Experimental Researches*, p. 905). The colour of the flame, viewed end on, was yellow, as if it contained sodium; but, on examining it with a spectroscope, it was found to give a continuous spectrum intersected by many shaded bands, and the D lines of sodium were only faintly present. The shaded bands were faint at a pressure of 5 atmospheres, but at pressures of 20 atmospheres and upwards they came out strongly. They were evidently the absorption bands of NO_2 , derived from the residue of atmospheric air mixed with the condensed gases. We took a photograph of them, and on comparing this with a photograph of the NO_2 bands, we found the two to be identical. Except for the bands, and the bright lines of sodium, the spectrum appeared to be continuous, and to extend from about λ 6200 to λ 4150, with the brightest part about λ 5150. It increased in brilliance as the pressure increased, as well as in extent, being visible at 3 atmospheres pressure from about λ 6720 to λ 4040. The greater distinctness of the NO_2 bands at the higher pressures was due both to the greater brightness of the continuous spectrum and to the greater quantity of NO_2 formed. A large quantity of water accumulated in the experimental tube, and when this was drawn off by the stopcock *s*, it effervesced with escape of

NO, and was found to be strongly acid. A specimen titrated was found to contain very nearly 3 per cent. of nitric acid. The observations were continued up to a pressure of 40 atmospheres. There was no indication that the continuous spectrum had any connexion with the line spectrum of hydrogen. There was no increase of brilliance in the neighbourhood of the C, F, or G lines of hydrogen. The characters of the spectrum were, however, better seen in the absence of NO₂, and will be described in the next section.

Oxygen Burning in Hydrogen.

In this case the colour of the flame was very different from that of hydrogen burning in oxygen. Instead of being yellow, it appeared, to the unaided eye, to have a lavender hue. In the spectroscope it shewed a perfectly continuous spectrum, brightest in the green, about the region of the Fraunhofer line *b*, and very gradually fading away on either side. On the red side it could be just traced up to about λ 6150, and on the violet side to about λ 4285, at ordinary pressures. The sodium lines were absent. With increase of pressure it increased very much in brightness, and at 8 atmospheres pressure it could be traced as low as λ 6630 and as high as λ 3990.

The dispersion used was that of a direct-vision spectroscope (such as was described by us, *supra*, p. 318), equivalent to three prisms of white flint glass, but the collimator and telescope very short, so as to obtain plenty of light. With less dispersion, perhaps, the continuous spectrum might have been traced further. Photographs, however, shewed that it scarcely extended into the ultra-violet. There was no indication that this spectrum was due to an expansion of the lines of either the first, or second, spectrum of hydrogen. It is true that the maximum brightness (which could not be determined with any great accuracy) was not very far from F, but no indication of any second maximum in the neighbourhood of either C or G, or anywhere else, could be detected. The pressure was carried up to 12 atmospheres, and at this pressure the visible spectrum was brilliant, but, in the ultra-violet, photographs shewed that the spectrum consisted only of what we have called the "water-spectrum," very strong and sharp. The lines of this spectrum shewed no signs of expansion even at a pressure of 12 atmospheres, and, though much more intense than at ordinary pressures, remained clearly defined.

Observations were continued with the eye up to 25 atmospheres pressure, but no trace of emission, or absorption, corresponding to either spectrum of hydrogen could be detected, and it is doubtful if either spectrum can be produced in such a flame. Since the formation of steam from its component gases is attended with a diminution of volume, increased pressure will increase the stability of the compound, and the flame will contain a larger

proportion of steam, as well as have a higher temperature, than at ordinary pressures.

The water formed when the flame was a jet of oxygen burning in hydrogen was found to be alkaline, and to contain ammonia. But the proportion of ammonia was much less than the proportion of nitric acid formed when the jet was hydrogen burning in oxygen; a specimen titrated contained 0.004 per cent. of ammonia.

Effects of Pressure on the Sodium Spectrum.

In order to see what effect would be produced by increased pressure on the spectrum of other substances in the flame, we charged the hydrogen with sodium vapour by making it pass, before entering the experimental cylinder, through a small iron cylinder, *e* in the figure, containing metallic sodium, heated by a lamp. As the D lines of sodium are very easily expanded and self-reversed in a flame at ordinary pressure, some care was needed to discriminate the effects which were really to be ascribed to pressure. The gas was easily charged with sodium vapour, and when burning in oxygen, not only the D lines, but the citron and green pairs, and sometimes the blue pair (λ 467), and the orange pair (λ 616), were well seen; but we could not find that they were expanded by increase of pressure. A sudden change of pressure generally produced an expansion, but it did not last; the lines fined down again when the pressure was steady, whether that pressure was high or low. These experiments were continued up to a pressure of 40 atmospheres without any definite effect on the width of the lines which could be ascribed to the pressure.

It may be said that at the higher pressure the evaporation of the sodium would be slower, and so the proportion of sodium vapour to hydrogen be diminished; also, when the lines are diffuse at the edges to begin with, it is extremely difficult to judge whether there is any expansion. At all events, we may say that there is no expansion produced by pressure at all comparable with that produced in a flame at ordinary pressure by increasing the quantity of sodium in the flame. We noticed, however, that the presence of sodium, which produces a feeble continuous spectrum in a flame at an ordinary pressure, seemed to increase the continuous spectrum of the flame under pressure, especially in the orange and green.

Oxy-hydrogen Jet in Carbonic Acid Gas.

For this experiment a two-branched tube (the upper one in the figure) was used. The jet of mixed oxygen and hydrogen was first lighted and introduced into the experimental cylinder while the latter was full of air and the stopcock *s* open. The air was then replaced by CO_2 entering by the tube *c*. The effect of this was at once to brighten the flame and change its

colour from yellow to blue. Seen in the spectroscope, the change consisted in an increase of continuous spectrum, especially towards the more refrangible end. When the stopcock *s* was closed so that the pressure rose in the experimental cylinder, the flame increased in brightness, but there was no other change in the spectrum. It remained continuous with no bright or dark lines, or bands, except the D lines of sodium. It resembled an ordinary flame of CO. The jet would not burn in CO₂ unless there was some excess of oxygen, and even with an excess of oxygen we could not get it to continue to burn in CO₂ at a pressure higher than 2 atmospheres.

Ethylene in Oxygen.

A jet of ethylene burning in oxygen gave, when the flame was small, the usual candle-flame spectrum, together with a band in the indigo ($\lambda 431$) shading towards the violet; but as the pressure was increased the continuous spectrum brightened and completely overpowered the bands, and at the same time the absorption spectrum of NO₂ appeared. We carried the pressure up to 33 atmospheres, and at that pressure the flame seemed to give nothing but a continuous spectrum, intersected by the absorption bands of NO₂. In our tube, the flame was viewed almost directly end on, and it is possible that if we had seen the flame sideways, we might have detected the hydrocarbon flame spectrum near the nozzle. At the high pressure much soot separated. We tried burning a mixture of ethylene and oxygen. The mixed jet burnt well in air and, when the supply of oxygen was sufficient, gave the hydrocarbon flame spectrum. In the experimental tube in oxygen, the jet burnt well at the atmospheric pressure, but we failed to get it to continue burning when the pressure was increased. The shaded band, commencing with a sharply-defined edge about $\lambda 431$, seems to be independent of the pressure, and has been before observed in a gas flame (Huggins, *Roy. Soc. Proc.*, Vol. xxx, p. 577). In fact, the only effect of pressure in this, as in the former cases, seemed to be the increase of the continuous spectrum.

Cyanogen and Oxygen.

As we could not obtain cyanogen at such pressures as we had used in the case of the other gases, we were obliged to content ourselves with exploding mixtures of cyanogen and oxygen in an iron bottle, fitted with a quartz stopper like that of the experimental tube above described. The bottle, having been exhausted by an air-pump, was filled with the mixture of gases, and exploded by an electric spark. With less than 3 vols. of oxygen to 1 vol. of cyanogen, there was always a considerable deposit of carbon, which covered the quartz and impeded vision; but, with 3 vols. of oxygen to 1 of cyanogen, the carbon was all burnt. Notwithstanding the brilliant banded spectrum of a flame of cyanogen in oxygen at ordinary pressure, nothing but a continuous

spectrum could be seen in the flash of the exploded gases, except the ubiquitous D lines of sodium. The continuous spectrum was bright. Photographs shewed a continuous spectrum with lines of iron, calcium, potassium, and sodium, but no cyanogen or carbon bands, or carbon lines. When a little hydrogen was added to the mixture of gases, no trace of the hydrogen red or green line could be detected in the spectrum of the exploding gas.

In every case, the prominent feature of the light emitted by flames at high pressure appears to be a strong continuous spectrum. There is not the slightest indication that this continuous spectrum is produced by the widening of the lines, or obliteration of the inequalities, of the discontinuous spectra produced by the same gases at lower pressures. On the contrary, it seems to be developed independently. This is, on the whole, quite in accordance with what would be expected, considering that under pressure the molecules of the gases have much less freedom, encounters amongst them are much more frequent, and they have much less chance of vibrating independently, and of taking up exclusively, or chiefly, the fundamental rates of vibration which are natural to them when free. Their condition, during a large part of any given time, approximates to that of the molecules of a liquid, and their spectra approximate to that of a liquid to at least a like extent. On the other hand, the higher temperature which, in many flames, attends an increased pressure ought to give some intensity to the special radiation which the molecules emit during their time of free motion; and this we have noticed to occur in the principal sections of the discontinuous spectrum of the oxy-hydrogen flame. Whether the continuous spectrum is due to the mutual action of the molecules of the compressed gases may perhaps be best determined by some photometric measures of the rate at which the brilliance increases with the pressure. Frankland (*Exp. Researches*, pp. 892 *et seq.*) has made some such measures, but not sufficient to solve the question. We have made an attempt to measure, not the total intensity of the light, but that of rays of definite refrangibility.

Photometry of Oxy-hydrogen Flame under Pressure.

The apparatus used for these measures was a spectro-photometer of the pattern employed by Crova (*Annales de Chimie*, ser. 5, Vol. xxix, p. 556). In this, the rays of one of the sources of light to be compared are passed through two Nicol prisms, and then reflected into one half of the slit of the spectro-scope, while the light from the other source passes directly into the other half of the slit. By turning one of the Nicol prisms, the light from the first source can be reduced at pleasure, and any small section of the spectrum can be separately observed by cutting off the rest by means of a shutter in the eye-piece. We found it by no means easy to get good concordant observations. A much larger vessel was used than for the earlier experiments, one

which contained several litres, and so we may presume a more uniform pressure was maintained within it. The results of the best series of observations on the photometric intensity of the jet of oxygen burning in hydrogen are given in the following table. The comparison light was a petroleum lamp.

1	2	3	4
15 lbs.	3°	274	$30 \times 3^2 = 270$
35	7	1485	$30 \times 7^2 = 1470$
55	11	3641	$30 \times 11^2 = 3630$
75	14	5853	$26 \times 15^2 = 5850$
95	19	10600	$29 \times 19^2 = 10469$

The first column gives the pressure of the gas, the second the mean of four to six observations of the angular deviation of the Nicol prisms from the position of complete extinction, for each pressure. The third column gives the squares of the sines of the angles in the second column multiplied by 100,000.

It will be seen from the last column that the numbers in the third column, which should be proportional to the photometric intensities at the respective pressures, are approximately proportional to the squares of the pressures.

This may be taken to indicate that the brightness of the continuous spectrum depends mainly on the mutual action of the molecules of gas.

A series of similar observations on hydrogen burning in oxygen gave somewhat different results, tabulated below:—

1	2	3
15 lbs.	6°	1093
35	13	5060
55	18	9549
75	22	14033
95	28	17861

The flame was brighter than that of oxygen burning in hydrogen at ordinary pressure, but the rate of increase with increased pressure was not so rapid as in the former case. It seems as if the continuous spectrum were made up of two parts, one varying as the square of the pressure, and another according to some other law. The flame is evidently not the same in the two cases. The products of combustion derived from the small quantity of air are different, and also the hydrogen jet always shewed the presence of sodium, sometimes calcium. The appearance of the flame was also different; the hydrogen jet being faintly visible and yellowish in the elongated part, whereas

the light from the oxygen jet was concentrated near the base, the point being invisible. The measures, of which the means are tabulated above, were also less concordant than the corresponding measures for the oxygen jet. We were unable to carry our measures beyond a pressure of 95 lbs., because at higher pressures a cloud was formed in the apparatus which prevented our seeing the flame directly. We hope to prosecute these measures with flames of other gases, and, if possible, at higher pressures.

The conclusions to which our experiments have led seem inconsistent with those which have been drawn from Plücker and Hittorf's well-known observations on the widening of the hydrogen lines in vacuous tubes with a residue of hydrogen when that residue increases. That the widening of the lines in a Plücker's tube results from increasing the density of the residue of hydrogen in the tube cannot be gainsaid, but we are wholly ignorant of the mechanism by which the gas is lighted up by the electric discharge. It is sometimes assumed, but without any sufficient reason, that the energy of the electric current is first converted into heat, and then in turn into radiation; but the electric energy may equally well be directly converted into the motion of radiation. As a fact, we have never yet been able to obtain either the emission or the absorption spectrum of hydrogen without the aid of an electric current, so that, in reasoning on this spectrum, we are much more in a region of speculation than when treating of flames. Whether the hydrogen lines, bright or dark, in the solar spectrum are produced directly by the high temperature of the sun, may even be called in question. And though we may admit that the density of the hydrogen in the sun's atmosphere, outside the photosphere, is but slight, it does not follow that the total pressure of all the gases forming that atmosphere is so very small as Messrs Frankland and Lockyer (*Roy. Soc. Proc.*, Vol. xvii, p. 288) have, from the width of the lines, concluded it to be. After all, it is not so easy to connect the temperature, even of a flame, with its radiation, for it is only when the condition of a gas is steady that we can assume that there is a definite relation between the motion of agitation, on which temperature depends, and the vibratory motions, on which radiation depends. In speculating on such questions, chemical, as well as electrical, changes must not be lost sight of, although the latter may be more directly concerned in radiation.

Experiments which we have commenced upon the arc in an atmosphere of compressed gas tend to the same conclusion. It does not appear that the metallic lines in the arc are sensibly affected by a steady pressure up to 15 atmospheres. The details of these observations, which are complicated by the variation of resistance with change of pressure, we defer until the experiments are finished.

NOTE ON THE SPECTRA OF THE FLAMES OF SOME METALLIC COMPOUNDS

[*Proceedings of the Royal Society*, Vol. LII. (1892), pp. 117 sqq.]

A STUDY of the spectra of flames offers many points of interest. It is long since A. Mitscherlich (Poggendorff's *Annalen*, Vol. cxvi, p. 499; Vol. cxxi, p. 459) shewed that the spectra of flames are, for the most part, those of compounds of the elements present, and contain comparatively few rays proceeding directly from the elements themselves. But there are many questions still undecided. For example, it is not known whether the vibrations which give the spectra of compounds in flames are those which the molecules of the compounds in question would assume under the action of a high temperature alone, or whether they are not vibrations of a different order, arising during chemical changes, and deriving their energy directly from the chemical energy of the interacting substances. When the absorption spectrum of a compound is observed to correspond with its emission spectrum in a flame, we may infer that the vibrations are those which the compound molecule assumes when sufficiently heated. But there are not many cases in which this has been observed. We have observed it in the case of cyanogen (*supra*, p. 242, and p. 370, note), but we are not certain of any other case. The difference between the spectrum of the base of a flame and that of the upper part, observed in many flames, lends support to the supposition that there are rays which originate in the chemical change, perhaps occurring in the molecules which are in intermediate stages of the change, and not assumed by the molecules which are the final product, even when intensely heated in the upper part of the flame. The fact that the same rays which are seen in the base of a flame may be sometimes generated by electric discharges in the gases which are burnt in the flame, or in their products of combustion, is not at all inconsistent with this supposition, for such discharges certainly have electrolytic effects, and may very well give rise to molecules in the intermediate stages between one state of chemical combination and another*.

* It is sometimes assumed in books on chemistry that the atoms which form a chemical compound can never be in an intermediate state between complete separation and complete combination. So inconceivable an assumption would hardly have been made except to support

The flames of substances, such as the organo-metallic compounds, into which metals enter as chemical ingredients, have not hitherto, so far as we know, been observed, and it is to two such flames that these notes refer.

Spectrum of the Flame of Nickel-Carbonyl.

The remarkable compound of nickel and carbonic oxide, $\text{Ni}(\text{CO})_4$, discovered by Mr Mond, burns in air with a luminous, smoky flame, and the spectrum it emits appears to be a continuous one. When the vapour is burnt in oxygen instead of in atmospheric air, the spectrum still appears to be quite continuous; in fact, such a spectrum as carbonic oxide, without any nickel, gives under similar circumstances. This, however, is only in appearance, because the brightness of the continuous spectrum overpowers the feebler bands and lines which belong to the flame of the nickel compound. These bands and lines come out when the vapour of the nickel compound is diluted with a good deal of hydrogen. We have employed two methods of making such a mixture. The first was by passing a stream of dry hydrogen, mixed with carbonic oxide, over reduced nickel in a glass tube, and burning the issuing gas in a double jet with oxygen either outside or inside the burning gas. The nickel was freshly reduced at a gentle heat with hydrogen, and allowed to cool in carbonic oxide. When quite cold the stream of mixed hydrogen and carbonic oxide was found to take up quite enough nickel at the temperature of the room, and would continue to do so for some hours. After a time, however, the nickel required to be again warmed in a current of hydrogen, when some water was given off, and the metal recovered its sensitiveness. Another plan was to pass a stream of hydrogen through a U-tube containing a little of the liquid nickel compound in the bend. The result was the same in each case, but the proportion of vapour of the compound was more easily varied (by simply varying the proportion of carbonic oxide in the stream of gas) in the former method. The mixed gas and vapour burnt in air with a smoky flame, but in a full supply of oxygen with a bright yellowish-green flame without visible smoke. The first jet we used was of platinum, but nickel-carbonyl deposits nickel at a red heat, so that the platinum soon became coated with a thick deposit of nickel, which choked the orifices. This nickel adhered so closely to the platinum that it could not well be removed mechanically, and had to be dissolved off. We found it, therefore, more convenient to use a jet made of a piece of porcelain tube, about 1 cm. in diameter, with a narrow porcelain tube, fitted by means of a cork, in the axis of the wider tube. The mixed gas and vapour were passed

a theory, but it has nevertheless obtained a certain currency. It is supported by no fact and no analogy. Two atoms which are within the spheres of each other's influence, but have not yet reached the state of relative tranquillity which we recognise as chemical combination, may very conceivably be the seat of very violent agitation and vibratory motions, which cease when they are actually combined.

either through the inner or through the outer tube, and oxygen through the other. The porcelain being a bad conductor, no nickel was deposited on it, except close to the orifice, whence it could be easily removed mechanically without disturbing the apparatus. The porcelain, of course, added some lines to the spectrum, but these were easily detected. In fact, we noticed only the lines of sodium, calcium, and lithium.

The spectrum of the flame of the nickel-carbonyl thus diluted consists of two parts: (1) the spectrum of the main body of the green flame, (2) that of the base of the flame when the oxygen is outside, and of the surface of the small inner cone when the oxygen is inside, the flame.

The spectrum of the main body of the flame consists of a series of shaded bands, brightest in the green, but extending on the red side beyond the red line of lithium, and on the violet side well into the blue, though with rapidly diminishing distinctness. These bands have their sharp bright edges on the more refrangible side, that is, they are turned in the opposite direction to the bands produced by electric discharges in carbonic oxide at low pressure. The positions of the bright edges of the bands in the flame of the nickel-carbonyl have some correspondence with those of the bands produced by electric discharges in carbonic oxide, but it is not a very close one, and may be only accidental. With the dispersion employed, which gives a difference of deviation of $2^{\circ} 52'$ between D and F, there was no sign of a resolution of these bands into lines. The brightest bands had, however, their more refrangible edges pretty sharply defined, while the less bright bands, especially those in the blue, were very hazy. A certain amount of continuous spectrum, of course, overlay the bands, and made them somewhat less distinct. Photographs shew that this continuous spectrum continues as far as λ 3500, but fades sensibly from λ 4200 onwards. The photographs do not shew any extension of the bands beyond the blue.

Besides the bands, a few lines, but only a few, in the visible part of the spectrum, extend into the upper part of the flame. Of these few only one is a known line of nickel; it is the green line λ 5476. This was also the only line of nickel which we observed in the visible part of the spectrum in explosions of hydrogen and oxygen in a nickel-lined tube (*supra*, p. 313).

In the ultra-violet part of the spectrum of the flame a great number of nickel lines were photographed; indeed, by far the greater part of the lines of nickel found by us in the arc (*supra*, p. 355) between λ 3972 and λ 2943.5. In this case also there is a close correspondence between the spectra of the flame and of the explosions, except that the lines of the flame are much more numerous than those recorded of the explosions. This difference, however, is probably due to the much shorter exposure of the photographs of explosions. Although the photographs shew lines

as high as λ 2943, the lines in this region are very faint, and gradually die out in proceeding from the less to the more refrangible side of the spectrum. In the region about L, M, and N the lines are very strong, so that it is for rays of those rates of vibration that nickel is most sensitive at the temperature of the flame.

Turning now to the base of the flame, we find a great number of lines, of which most extend but a short distance from the bottom of the flame. They form two principal groups, one in the orange and red, and the other in the citron and yellow. These lines are for the most part sharply defined, and in the more refrangible parts of each group very fine and closely set. They are probably channellings following Rydberg's law, and somewhat confused by overlapping. The diagram indicates the strongest of these lines, as they appear on the background of shaded bands in the flame. It is drawn to a scale of oscillation frequencies.

None of these lines appear to be nickel lines, and, as they are limited to the base of the flame, they cannot be ascribed to any of the final products of the combustion, such as nickel oxide, but must be due either to the as yet unaltered molecules of nickel-carbonyl, or to some molecules intermediate between that compound and the products of combustion which have only a transitory existence, and may perhaps have a transitory agitation of a particular kind imparted to them by the chemical energy which changes its form in the combustion.

The following tables give the approximate oscillation frequencies of the edges of the principal shaded bands, and of the lines seen at the base of the flame, but the numbers are only approximate.

Oscillation Frequencies of Edges of Shaded Bands.

1496	1692	1933	2146
1521	1752	1960	2172
1577	1808	2052	2199
1594	1849	2107	2226
1635			

Oscillation Frequencies of Lines in the Base of the Flame.

1497	1547	1580	1598
1506	1549	1582	1599
1509	1555	group of very	1600
1514	1560	closely set lines	1602
1518	1563	1586	1604
1521	1572	1593	1607
1526	1575	1595	1612
1543	1578	1596	1615

Oscillation Frequencies of Lines in the Base of the Flame (*continued*).

1616	1671	1721	1746
1618	1673	1727 <i>l</i>	1747
1622	1682	1732 <i>l</i>	1753
1627 <i>l</i>	1686	1735	1806
1631 <i>l</i>	1690 <i>l</i>	1738	1809
1651	1706	1741 <i>l</i>	1827
1656	1712	1742	1833
1663	1714	1745	1879
1667	1716		

The six numbers in the above table to which an *l* is added correspond to lines which extend into the upper part of the flame.

Table of Wave-lengths of Nickel Lines photographed from the Flame.

2943·5	3183·8	3390·4	3561·1
2981·2	3194·9	3392·4	3565·7
2983·6	3196·6	3409·0	3571·2
2992·2	3201·5	3413·4	3587·2
2994·1	3221·1	3413·8	3601·4
3002·1	3224·6	3423·1	3609·8
3003·2	3226·3	3433·0	3612·1
3011·5	3232·6	3436·7	3618·8
3018·8	3234·2	3445·7	3624·1
3031·4	3242·6	3452·3	3663·4
3037·5	3247·8	3457·8	3669·7
3044·5	3250·1	3461·1	3673·4
3050·4	3270·6	3466·8	3687·6
3053·9	3282·2	3468·9	3694·6
3057·2	3285·0	3470·8	3721·6
3064·2	3315·1	3483·1	3736·1
*3080·3 ?	3319·7	3485·2	3737·0
3096·6	3321·6	3492·3	3745·0
3098·6	3361·0	3500·0	3775·0
3101·1 }	3365·5	3509·7	3783·0
3101·4 }	3367·2	3514·4	3791·0
3105·0	3368·9	3519·1	3806·6
3113·7	3371·3	3523·9	3831·7
3133·6	3373·6	3527·1	3857·8
3145·5	3380·0	3547·5	3972·0

* A query is placed against this number because the water spectrum is so strong at this point that we cannot certainly distinguish the nickel line. There is no other reason for doubting its presence.

The more refrangible lines in the foregoing table were very faintly depicted on the photographic plate, and it is possible that a more lengthened exposure than the fifteen minutes, which we employed in the region where the lines were faint, would have brought out more lines. The continuous spectrum of the limelight extends some distance further than the most refrangible of these nickel lines.

Flame of Zinc Ethide.

Zinc ethide burning undiluted produces so much continuous spectrum as to overpower any special rays. But by passing a stream of hydrogen through a bent tube containing zinc ethide, and burning the mixed gas and vapour in oxygen, as we did the nickel-carbonyl, we reduced the continuous spectrum sufficiently to enable us to observe any fairly strong rays which might be peculiar to the flame. In the visible part of the spectrum the three well-known rays of zinc in the blue λ 4812, 4721, and 4681 were easily seen. Photographs of the more refrangible part of the spectrum shewed no trace of the ultra-violet lines of zinc; no more, in fact, than the flames of hydrocarbons usually shew. Nor did there appear to be any rays from the base of the flame other than those seen in hydrocarbon flames in general. In our observations on explosions (*supra*, p. 312) we did not find that a zinc lining to the tube in which the oxy-hydrogen gas was exploded brought out any zinc line, either in the visible or ultra-violet part of the spectrum. The flame of the compound containing zinc chemically combined may be supposed to give the rays of zinc more readily than the exploding gases, which merely take up the metal mechanically. But the flame does not, in either case, seem hot enough to develop the ultra-violet rays, though these are very strongly developed in the arc.

ON THE SPECTRUM OF LIQUID OXYGEN, AND ON THE REFRACTIVE INDICES OF LIQUID OXYGEN, NITROUS OXIDE, AND ETHYLENE

[*Philosophical Magazine*, Ser. 5, Vol. xxxiv. (1892), pp. 205 sqq.]

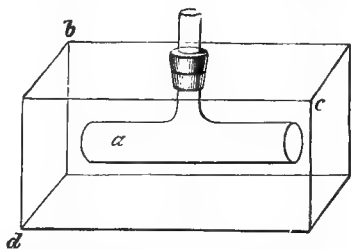
IN September 1888 we described in this Magazine (*supra*, p. 377) the absorption-spectrum of oxygen gas in various states of compression. At lower pressures the absorptions known in the solar spectrum as A and B were most conspicuous, and as the pressure increased the other bands described by Janssen came out with increasing intensity. The former appear to be due to the molecules of oxygen, and increase in intensity directly with the mass of the oxygen producing them; while the latter appear to arise from the mutual action of the molecules on one another, since their intensity is dependent on the density as well as the mass of the oxygen producing them.

With the small dispersion employed in these observations the absorptions A and B were not resolved into lines as in the solar spectrum, but they had otherwise the same general characters: A consisted of two bands, and both A and B were sharply defined on the more refrangible edge and gradually faded out on the less refrangible side. Considering how much more diffuse the lines forming these groups in the solar spectrum become as the sun gets nearer the horizon (see McClean's photographs), it is probable that, under the circumstances of our experiments, they would not have been resolvable into lines even with higher dispersion.

Subsequently, in a paper read at the Royal Society (*supra*, p. 385), we described our observations on the absorption of a thickness of 12 millim. of liquid oxygen. We noticed, as Olszewski had done, the strongest three of the diffuse bands seen in the spectrum of the compressed gas, but could not detect A. The mass of oxygen in 12 millim. of the liquid was not enough to make A visible.

We have since made observations with larger quantities of liquid oxygen. For this purpose we have used a glass tube of the form shewn at *a* in the annexed figure, about $\frac{3}{4}$ inch in diameter and 3 inches in length. This tube had the ends blown as flat and clear as possible, and it was enclosed in a box

b c d with glass sides, and the air in the box well dried, in order to prevent the deposition of hoar-frost on the tube. The liquid oxygen was poured into the tube at the pressure of the atmosphere, and at first, of course, boiled violently, until the tube was reduced to the temperature of boiling oxygen, -181° , after which the liquid boiled slowly and quietly. Through the length of the tube (that is, a thickness of about 3 inches of liquid oxygen) we viewed the hot pole of an electric arc with a spectro-scope having two calcite prisms of 30° and one of 60° . As reference-rays we used the red potassium-lines, of which the positions with reference to A and B were well determined by Kirchhoff, and confirmed by our own observations. These lines were easily obtained by dropping a little of a potassium salt into the arc.



The diffuse bands previously seen both in the gas and liquid were all of exceptional strength, but we did not notice any addition to their number except a faint band just above G. In place of A we observed a band, but different from A in the following remarkable particulars. Instead of having a sharp edge on the more refrangible side and fading gradually towards the less refrangible side, its position appeared to be reversed; the sharp edge was on the less refrangible side, and it faded away gradually on the more refrangible side. Moreover its sharp, less refrangible edge did not coincide with the sharp edge of A, but reached very nearly to the more refrangible of the two potassium-lines, that is, had a wave-length of nearly 7660. At the same time the band extended beyond the sharp edge of A on the more refrangible side. There was no indication that it was resolvable into lines, or even into two bands. Turning to the place of B in the spectrum we were not able, with that thickness of oxygen, to detect any band in that place. Olszewski (*Wied. Ann.*, New Ser., Vol. xlii, p. 663), with a thickness of 30 millim. of liquid oxygen, observed a somewhat faint band corresponding to A, which with a Rutherford prism was not resolvable into lines, but he has not noticed the reversed position of the band.

Using a similar tube for the liquid oxygen, but six inches long, the band at A came out very much stronger and extended much further on the more refrangible diffuse side, but was not conspicuously expanded on the other side, and did not hide the potassium-line. At the same time a fainter band appeared at the place of B. This had precisely the same character as that at A; that is, it had its sharp edge on the less refrangible side and faded gradually on the more refrangible side. Its sharp edge also did not coincide with the sharp edge of B, but reached nearly to the red potassium-line $\lambda 6913$. By estimation, using the potassium-lines for comparison, we put the wave-length

of the less refrangible edge at about λ 6905, while its diffuse side was visible to about λ 6870, that is, barely to the place of the strong edge of B.

It is plain that these two bands are related to each other in the same way as the solar groups A and B are related, and we cannot avoid the conclusion that they represent A and B, but modified by the change of the absorbent from the gaseous to the liquid state.

If, as there is good reason to think, A and B are the absorptions of free molecules of oxygen, the persistence of these absorptions in the liquid seems to shew that the molecules in the liquid are the same as in the gas. At the same time the changes they undergo ought to throw some light on the nature of the change in passing from the gaseous to the liquid state, as well as on the causes which produce the sequences of rays which are called channelled spectra.

We have noticed, as Olszewski also has noticed, that liquid oxygen is distinctly blue. This is, of course, directly connected with its strong absorptions in the orange and yellow. On looking at a mass of liquid oxygen through a direct-vision spectroscop in any direction the scattered light shews the strong bands plainly. Indeed they remain visible when the oxygen has evaporated to the last drop, and they increase in intensity as the liquid is cooled, so that when the pressure on the liquid is reduced and the oxygen cooled by its own evaporation to -200° they become exceedingly black. Olszewski states that this blue colour is not, so far as he could make out, due to ozone, and we are of the same opinion. Ozone dissolves easily in liquid oxygen and imparts to it an indigo-blue colour. Such a solution when poured into a saucer of rock-salt assumes the spheroidal state, and as the oxygen evaporates becomes more concentrated, and finally explodes with considerable violence. In the dilute solution we could not detect any absorptions due to the ozone. We attempted to obtain a larger quantity of liquid ozone, or of a concentrated solution, for the observation of its spectrum. Oxygen ozonised in a tube cooled by solid carbonic acid gave small beautiful cobalt-blue drops of liquid, but when a few of these drops collected together in a tube immersed in liquid oxygen to cool it to -181° , they exploded and blew the whole apparatus to pieces, comminuting the tube to fine powder. This instability of ozone, equally at very low and at high temperatures, is a significant fact in regard to the form of chemical energy. It seems probable that it is connected with the great absorbent power of ozone. The radiant energy absorbed must give rise to molecular movements which may, we conceive, set up disintegration.

The determination of the refractive index of liquid oxygen, at its boiling-point of -182°C. , presented more difficulty than would have been anticipated. The necessity for enclosing the vessel containing the liquid in an outer case to prevent the deposit of a layer of hoar-frost which would scatter all the rays

falling on it, rendered manipulation difficult; and hollow prisms with cemented sides cracked with the extreme cold. It was only after repeated attempts, involving the expenditure of a whole litre of liquid oxygen on each experiment, that we succeeded in getting an approximate measure of the refractive index for the D line of sodium. The mean of several observations gave the minimum deviation with a prism of $50^{\circ} 15'$ to be $15^{\circ} 11' 30''$, and thence $\mu = 1.2236$. The density of liquid oxygen at its boiling-point of -182°C . is 1.124, and this gives for the refraction-constant, $\frac{\mu - 1}{d} = 1.989$, and for the refraction-equivalent 3.182. This corresponds closely with the refraction-equivalent deduced by Landolt from the refractive indices of a number of organic compounds. Also it differs little from the refraction-equivalent for gaseous oxygen, which is 3.0316. This is quite consistent with the supposition that the molecules of oxygen in the liquid state are the same as in the gaseous.

If we take the formula $\frac{\mu^2 - 1}{(\mu^2 + 2)d}$ for the refraction-constant we find the value of it for liquid oxygen to be .1265, and the corresponding refraction-equivalent 2.024. These are exactly the means of the values found by Mascart and Lorenz for gaseous oxygen. The inherent difficulties of manipulation, and the fact that the sides of the hollow prism invariably became coated with a solid deposit, perhaps solid nitrogen, which obscured the image of the source of light, have hitherto prevented our determining the refractive indices for rays other than D*.

The determination of the refractive indices for liquid nitrous oxide did not present so great difficulties. The minimum deviations for the rays C, D, F, G, and for the lithium ray $\lambda 6705.5$, and the indium ray $\lambda 4509.6$, were found to be, respectively, $22^{\circ} 53'$, 23° , $23^{\circ} 18'$, $23^{\circ} 33'$, $22^{\circ} 52'$, and $23^{\circ} 28'$. The corresponding values for μ are 1.329, 1.3305, 1.3345, 1.3378, 1.3257, and 1.3368.

The specific gravity of liquid nitrous oxide at its boiling-point of -90°C . was found, by weighing 100 cubic centim. of the liquid, to be 1.255.

This gives, for the D ray, $\frac{\mu - 1}{d} = 0.2634$ and for the molecular refraction 11.587. Or, if we take the other formula, $\frac{\mu^2 - 1}{(\mu^2 + 2)d} = .163$ and the corresponding molecular refraction 7.163. Subtracting the refraction-equivalent

* This will be prosecuted further, however. The refractive index of oxygen has an important bearing on the electro-magnetic theory of light, considering that we are dealing with a magnetic liquid. The polarizing angle corresponding to the index of refraction found above for liquid oxygen is $50^{\circ} 45'$, and one of us has found that when liquid oxygen is cooled to -200° by its own evaporation at reduced pressure so as to present a steady surface, and the image of a candle is viewed by reflexion at that surface, the light is very completely polarized when the incidence is at that angle.

for oxygen we get for the molecular refraction of nitrogen 8.405 or 5.139 according to the formula used. Mascart's determination of the index of refraction of gaseous nitrous oxide for the D ray was 1.000516 and the corresponding molecular refraction 11.531, or 7.69, according to the formula used; and in this case the older formula for the refraction-equivalent satisfies the condition of continuity between the gaseous and liquid states better than the newer.

It was more difficult to obtain the refractive indices for liquid ethylene on account of its irregular boiling. Liquid oxygen and nitrous oxide boil steadily, but ethylene in sudden bursts of large volumes of vapour. The minimum deviation for the D ray was found to be $25^{\circ} 29'$, approximately. This gives $\mu = 1.3632$, and, since the density of the liquid at its boiling-point of -100°C. is 0.58, $\frac{\mu - 1}{d} = 0.672$ and $\frac{\mu^2 - 1}{(\mu^2 + 2)d} = 0.384$. The corresponding numbers for gaseous ethylene, according to Mascart, are 0.578 and 0.385. The agreement for the second formula is close, but we doubt if much stress can be laid on this, inasmuch as we know that the liquid ethylene contained a small quantity of ether.

NOTE ON PLÜCKER'S SUPPOSED DETECTION OF THE LINE-SPECTRUM OF HYDROGEN IN THE OXY-HYDROGEN FLAME

[*Philosophical Magazine*, Ser. 5, Vol. xxxiv. (1892), pp. 371 sqq.]

IN a paper published in Poggendorff's *Annalen* (1862, 4th ser., Vol. xxvi, p. 48) Plücker stated that the flame of a mixture of oxygen and hydrogen, when the latter was slightly in excess, shewed the two lines of hydrogen H_{α} and H_{β} .

The passage in which this statement occurs is an episode in a paper on recurrent electric discharges in gases at low pressure, and is given by way of confirmation of the author's theory that the illumination of gases by the electric discharge is due to the high temperature of the discharge.

This statement seems to have been generally accepted on Plücker's authority; but no one else, so far as I can learn, has ever succeeded in seeing, or in photographing, any of the lines of hydrogen in the spectrum of a flame. Nevertheless no one has, I believe, distinctly challenged the correctness of the statement, and it is still currently taken to be true, and inferences have been drawn from it (as to the condition of the solar atmosphere and other matters) which become untenable if Plücker was mistaken. Plücker's authority is so great that every one hesitates to call any observation of his in question. Moreover, it is difficult to prove a negative. For one to succeed with an experiment when another fails is nothing uncommon. Still spectroscopy has made long strides since 1862, and the interests of science demand that the evidence on this question should be reviewed.

Two years after the publication of Plücker's paper, Dibbitts, also a good observer, published in the same journal (*Pogg. Ann.*, 5th ser., Vol. ii, p. 497) an account of his observations of the spectrum of the flame of hydrogen burning in air, in oxygen, in nitrous and in nitric oxides, and in chlorine. In every case he found it to be a faint continuous spectrum extending from red to blue, fading out at both extremities, and brightest in the green. No line but the yellow line of sodium was to be seen, except when he used jets of brass. Even in this case it was not until the metal had become a little oxidized that any lines were visible. When this occurred several bright lines

were seen in the red, green, and blue, and the brightest of them he found to be identical with those produced by copper chloride in the flames of a Bunsen burner.

In 1868 (*Proc. Roy. Soc.*, xvi, p. 421) Frankland stated that he had observed the combustion of hydrogen in oxygen under a pressure gradually increasing up to ten atmospheres; and that at the last-named pressure the spectrum of the flame was perfectly continuous. He does not say what it was at the lower pressures. Salet also (*Compt. Rend.*, lxxiii, p. 404) says that hydrogen burnt in oxygen gives a continuous spectrum.

Some years ago, when examining the spectrum of the arc in hydrogen, given by a powerful dynamo, I was struck by the fact that no line of hydrogen, bright or reversed, could be detected, except at the moment of breaking the arc. This led me to look at the oxy-hydrogen flame; when I found, to my surprise, that the hydrogen lines were absent from the flame. Subsequently (*supra*, p. 89) Dewar and I found that the alternating current from a De Meritens magneto-electric machine, arranged for high tension, produced an arc in hydrogen which shewed H_{α} fairly bright and H_{β} as a faint diffuse band. Secchi (*Compt. Rend.*, lxxvii, p. 177) stated that the negative pole of an arc shewed lines of hydrogen and of the metals in the carbons, and that a drop of water thrown on the carbons caused the hydrogen-lines to appear, and many others. Subsequently we found (*supra*, p. 268) that when a small drop of water was let fall into the arc given by a dynamo machine, both H_{α} and H_{β} were visible in the spectrum for an instant.

Since then I have made a very great many observations of the spectrum of the oxy-hydrogen flame, both directly and by photography, but have never met with a trace of the hydrogen-lines in the flame. The jets used, the proportions of the two gases, and their pressures have been varied in all sorts of ways, but with the same negative result as regards the line-spectrum of hydrogen. In particular, when mapping the spectrum we have ascribed to water (*supra*, p. 322) I took a great many photographs of the spectrum of the oxy-hydrogen flame, at atmospheric pressure, in the region from about λ 350 to λ 450, with exposures of three hours, and in a few cases even longer, but no one of these shewed a trace of the hydrogen-lines H_{γ} , H_{δ} , or H_{ϵ}^* . Other photographs of the spectrum of the flame extended as low as D, but these likewise shewed no trace of any hydrogen-line. If the rays were emitted at all by the flame, though so faint as not to be detected by the eye, they must surely have depicted themselves on the photographic plate with so long an exposure.

However, it might have happened, though it is not likely, that there was

* This is following Plücker's notation, so that H_{ϵ} stands for the hydrogen-line corresponding to the Fraunhofer line H.

something in Plücker's arrangement which had enabled him to get the lines, while I failed. So I have made a new series of direct observations of the flame in order to make sure. Unfortunately, Plücker's mention of his observations is an episode, and he does not describe his apparatus. He merely says that he allowed the two gases, from two gasometers, to flow together, and inflamed them, and endeavoured so to regulate the pressure that the *excess* of hydrogen should be heated as much as possible by the flame. He succeeded in getting a red tip to the flame, and a Babinet's goniometer shewed H_{α} and H_{β} .

I have tried three forms of jet, all of platinum. First a double jet, one tube within the other, and hydrogen supplied through the inner tube, oxygen through the outer; also the same with hydrogen outside and oxygen inside. Secondly, a jet in which the two gases were mixed in a small chamber, and the jet of mixed gas burnt. Thirdly, two streams, one of oxygen and the other of hydrogen, were allowed to impinge on one another at an angle of about 45° , so as to form a fish-tail flame.

I used two spectroscopes. The telescopes of one had object-glasses $2\frac{1}{4}$ inches in diameter, with two prisms of 30° of similar aperture, fixed one in front of each object-glass and carried with the telescope, so that the spectrum was always of the greatest purity and the light ample. I used also an eye-piece of low power, so as to have every chance of detecting faint lines.

The other was smaller. It was a direct-vision spectroscope with two Christie half-prisms, of which the second was in the reversed position, so as to give a pure spectrum though no great dispersion: an excellent instrument for detecting faint diffuse lines or bands.

In observing, the instrument was set and focused for the F, or C, line of the solar spectrum, and then turned to the flame, and the room darkened.

In every case the proportion of oxygen to hydrogen was very gradually varied, from excess of hydrogen to excess of oxygen and *vice versa*; and different parts of the flame brought in front of the slit. This was done again and again, but no trace of any hydrogen-line could be detected. Except for the D line of sodium, which was always present, and flashed out brightly as particles of dust entered the flame, and for an occasional flash of the two well-known lime-bands, the spectrum was quite continuous, extending from near C to near G, very faint at both ends.

When the hydrogen was in excess the flame had a reddish tip, which may be what Plücker saw; but the spectroscope shewed that this colour was only due to the fact that (under these conditions) the maximum of the continuous spectrum lay in the orange between C and D. This continuous spectrum

faded away gradually and could be traced down to about the position of C, but there it ended, and there was nothing like a maximum at C. When the oxygen was in excess the maximum of the continuous spectrum shifted into the citron, and I could no longer trace the spectrum so low as C. There was no maximum of brightness about F or G'.

When the separate impinging jets were used the flame had a curious appearance—the oxygen side had a greenish hue, the hydrogen side a fainter orange hue. In the mid-plane would be the most active combustion and the hottest temperature, and there, if anywhere, we might expect to see the hydrogen rays developed. I examined both the broad side and the edge, but could see no hydrogen-line at all. When the spectroscope was directed on to the edge, the radiation would be received from a considerable thickness of the hottest part of the flame, and this would seem to be the most favourable condition for detecting the hydrogen rays.

Having failed to get the hydrogen rays at all in any of these flames I next tried a cyanogen flame burning in oxygen, and introduced a very small jet of hydrogen into the middle of the flame. The cyanogen flame in oxygen is much hotter than the hydrogen flame, and gives a brilliant spectrum of channellings. The flame, however, has a very definite inner cone which gives this bright spectrum, while the flame outside the cone hardly shews any of it. The introduction of the smallest quantity of hydrogen alters the general appearance of the flame, but seems to alter the brightness only of the spectrum. No hydrogen-line could be detected in the spectrum of the cone, or the flame above it. One of the channellings in the spectrum of the cone overlaps the place of H_{α} , so that it might be difficult to detect H_{α} if it were present, except in the part of the flame above the cone; but there is a gap in the channellings about H_{β} , so that line could be seen easily if it were present. But I could not detect it.

After such a series of negative results I can only come to one conclusion, namely, that the temperature of the oxy-hydrogen flame alone is not sufficient to cause hydrogen to emit the rays we see produced by an electric discharge in that gas, and that Plücker must have mistaken some other rays for those of hydrogen. What those rays probably were it is almost impossible to say with the very scanty information he has given. If the hydrogen he used were generated in the gasometer, it may have had some fine spray of a zinc solution mixed with it. Such a spray in an oxy-hydrogen flame may, under favourable circumstances, give a spectrum of three blue lines, of which the least refrangible is the strongest and has a wave-length about 4810. A little zinc-ethyl in the hydrogen gives them well. Plücker does not say how he identified the rays he saw with H_{α} and H_{β} , but if he did not make a direct comparison, and if his Babinet's goniometer had, as is probable, only a single prism, it is possible that he might have mistaken the zinc-line for H_{β} . An electric spark taken from a solution of zinc gives also a red line, but this line

is not, so far as I have observed, produced by zinc in any flame, so it will not account for the line set down as H_{α} . The only suggestion I can offer for the red line is that it may have been the red line of lithium. Lithium dust may easily have been present in the laboratory, especially if a flame with lithium in it had recently been employed; and, as the dispersion of a single prism in the red is but small, it is just possible that in a hasty examination the lithium-line may have been mistaken for H_{α} . I am very unwilling to accuse such an observer as Plücker of the carelessness which is implied in the supposition that he mistook the lithium-line for hydrogen, and should not think of doing so if his whole account did not appear to be given merely by the way in support of a theory which is not now generally accepted. There remains the supposition that he used, as Dibbits did, a jet of brass, or of some other metal, which gave its own lines in the flame.

ON THE REFRACTIVE INDICES OF LIQUID NITROGEN AND AIR

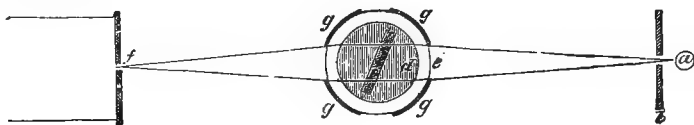
[*Philosophical Magazine*, Ser. 5, Vol. xxxvi. (1893), pp. 328 sqq.]

IN describing the spectrum of liquid oxygen (*supra*, p. 412) we gave a determination of the refractive index of that liquid, and of those of some other liquefied gases, for the D ray. The difficulty of such measurements was mainly the mechanical one of making a hollow prism with truly wrought faces which would stand the extreme cold, and not convey heat from outside to the liquid within so fast as to keep it in rapid ebullition. The dispersion of the light by the bubbles passing through the liquid is sufficient to blur the image of the source of light, so much as to render an accurate measurement of the dispersion almost impossible. And though by diminishing the pressure, and thereby causing a rapid evaporation, the liquid oxygen can be reduced to -200°C . and then remains quite tranquil, this was found to be of little avail; for it involved the use of a hollow prism capable of holding rather a large bulk of liquid, and of sustaining variation of pressure as well as of temperature without leaking. We had therefore to turn our attention to other methods of determining refractive indices. Of these the method used by MM. Terquem and Trannin seemed to be most free from difficulty, and had been successfully employed in the determination of the refractive index of liquid oxygen by Olszewski and Witrowski, whose value of the index agreed with ours found with a prism (*Bull. de l'Académie de Cracovie*, 1892, p. 341). This method consists in suspending in the liquid two plates of glass with a thin layer of air between them, and measuring the angle of incidence at which the chosen ray suffers total reflexion at the surface of the air.

In this method it is not necessary that the vessel containing the liquid should have truly wrought surfaces, and the problem seemed to be simplified by the discovery of Professor Dewar that the amount of heat communicated to the vessel of liquid by radiation is trifling compared with that communicated by convection. He has found that in a double glass vessel of any form, where the outer and inner vessels are separated by even a narrow vacuous space, liquid oxygen can be kept for a great length of time open to the air.

Such a liquid, filtered through ordinary filter-paper to remove solid carbonic acid, remains quite tranquil and beautifully transparent of pale blue tint, but of course evaporating gradually and generally giving off streams of small bubbles. These bubbles do not sensibly mar the distinctness of an object viewed through the liquid with the naked eye, but we found that they did make a difference when a telescope was used. As we had no double vessels with a vacuous interval except such as were either globular or cylindrical, we had to meet the difficulty that such vessels when filled with liquid acted like lenses, and lenses which were irregular and full of striations. In fact we could not by the use of compensating lenses obtain in the field of a small telescope any tolerably definite image of a candle, or other source of light, seen through the vessel. At the same time, when the pair of glass plates above mentioned was suspended in the liquid and a sodium-flame viewed with the unaided eye through them, the extinction of the light, when the plates were turned to the position for total reflexion, appeared quite sudden. The use of a telescope, however, shewed that the rays forming the blurred image, even when limited by screens to the central part of the globe, or cylinder, really passed in so many different directions that they were by no means all extinguished at once.

In order to avoid the necessity of observing any image at all through the liquid, we made use of it simply as a lens to concentrate the light observed on the slit of a spectroscope. The arrangement is shewn in the annexed figure, where *a* is the source of light, either a sodium-flame or an electric



spark, *b* a screen with a slit, *c* the outer glass vessel, *d* the inner glass vessel with the liquid, *e* the pair of glass plates immersed in the liquid, *f* the slit of a spectroscope, *gg* screens of black paper on the outside of the outer vessel.

The distances of *a* and *f* were arranged so that they should be conjugate foci when the vessel was midway between them. The pair of glass plates were separated by a narrow ring of thin filter-paper, thoroughly wetted with white of egg and allowed to dry. They were held in a small brass clip attached to a rod, which formed the prolongation of the vertical axis of a theodolite, by which the angle through which they were turned was measured. They were adjusted to the vertical plane by observing with a cathetometer the reflexion at their surface of a flame which had been adjusted to lie in the same horizontal plane as the centre of the plates.

The arrangement was tested by the measurement of the refractive indices, for the D ray, of water and of alcohol, contained in one of the same double

vessels which were subsequently used for liquefied gases. The results were satisfactory, though, owing to the irregular form of the vessels and the striæ on their surfaces, the extinction of the light on turning the plates was hardly so sudden as we had expected. The angles were measured by first turning the pair of plates in one direction until the ray under observation was extinguished, and reading the position on the graduated circle of the theodolite, and then turning the pair of plates in the opposite direction until the ray was again extinguished, and again reading the circle. The angle between the two positions was the double of the angle required, namely the angle of incidence for total reflexion of the ray observed.

Trying the apparatus with liquid oxygen, we found that the extinction of the ray was less sudden than with either water or alcohol. This was no doubt caused by the small bubbles which scattered the light. Nevertheless it was easy to trace the passage of commencing obscurity from the blue to the red end of the spectrum as the plates approached the positions of total reflexion. Hence approximate values could be found for the indices of refraction for the D ray. In this way liquid oxygen gave $\mu = 1.226$, a slightly larger value than that we had found with the prism, which was 1.2236.

We then tried liquid nitrogen at its boiling-point of -190°C . at atmospheric pressure. The mean of six readings gave for the D ray $\mu = 1.2053$. The nitrogen was not quite pure, but contained about 5 per cent. of oxygen, notwithstanding that it had been passed before compression through a stack of tubes filled with copper and heated red-hot. We have no reason to think that this small quantity of oxygen had any other effect than to increase the index of refraction by a very small quantity.

Liquid air was next observed. The mean of ten measurements gave for the D ray $\mu = 1.2062$. With liquid air the evaporation of the more volatile nitrogen goes on more rapidly than that of the oxygen, so that the liquid gradually gets stronger in oxygen, until at last there is little but oxygen left. Liquid nitrogen is colourless, and the colour of liquid air is merely that of the oxygen it contains. Further observations with the liquid air when a good deal of nitrogen had evaporated gave $\mu = 1.215$; and when still more nitrogen had gone we found $\mu = 1.218$.

The value found above for the refractive index of liquid nitrogen at -190°C . when it has, according to Prof. Dewar's observations, a density of .89, gives for the refraction-constant $\frac{\mu - 1}{d} = 0.225$, and for the refraction-equivalent 3.153.

If we take Mascart's value of μ for gaseous nitrogen, namely 1.000298, and the density at .001256, we get for $\frac{\mu - 1}{d}$ the value 0.237, which agrees well with that found above for the liquid.

If we take Lorenz's formula $\left(\frac{\mu^2 - 1}{\mu^2 + 2}\right) \frac{P}{d}$ for the constant of refraction, we get the value for liquid nitrogen 0.1474 and the refraction-equivalent 2.063.

Brühl's values of the refraction-equivalent, derived from observations of the compounds, were for free nitrogen 2.21, for nitrogen as in nitrous oxide 2.27 at least, and for nitrogen as in ammonia 2.50. These numbers are somewhat larger than ours, but not a great deal. On the other hand, Gladstone's value for nitrogen in nitriles was 4.1 and in ammonia 5.1, which differ a good deal from our value, using Gladstone's formula, namely 3.153.

We hope in a short time to give the refractive indices for other rays, and the dispersive powers, of liquid oxygen, nitrogen, and air at a temperature as low as -200°C .

PRELIMINARY NOTE ON THE SPECTRUM OF THE ELECTRIC DISCHARGE IN LIQUID OXYGEN, AIR, AND NITROGEN

[*Philosophical Magazine*, Ser. 5, Vol. XXXVIII. (1894), pp. 235 sqq.]

IN making the experiments here described we desired, if possible, to observe the emission-spectra of the several substances, stimulated by the electric discharge, while at temperatures of 180° to 200° below zero. It seemed probable that the characters of these spectra would give some indications of the physical state of the substances operated on.

In order to prevent the rapid heating of the electrodes by the discharge, they were made of considerable size. One was a disk of platinum about one centimetre in diameter, convex on one side, and having its convexity turned towards the other electrode, which was made of a piece of platinum wire about two millimetres thick. Even these electrodes were much heated, became red-hot when they were not in the liquid but the spark passed through the gas immediately above the liquid. When actually immersed in the liquid they could hardly have been, except locally at the point of discharge, at any temperature sensibly different from that of the liquid. Experiments were made also with electrodes of aluminium, but with no different results as regards the spectrum except the introduction of the shaded bands due to alumina instead of the lines of platinum.

The liquids experimented on were contained in double test-tubes of large dimensions, having the space between the two tubes highly exhausted. The electrodes, insulated, except at the extremities, by glass tubing and wax or gutta-percha, were passed through a rubber-stopper which closed the tube. Through this stopper was also passed a glass tube, which was left open while experiments were made at the atmospheric pressure, but was connected with a powerful rotary air-pump when it was desired to exhaust the gas in the tube.

Liquid oxygen, air, and nitrogen, like non-electrolysable compound liquids, offer very great resistance to the passage of an electric discharge, so that with a powerful induction coil we could hardly make the spark pass through a thickness of one millimetre of liquid. When the thickness of liquid traversed

was less than this, a succession of sparks could be maintained; but the resistance appeared to be very great, and the disruptive effect on the electrodes sufficient to discolour the liquid by the particles thrown off their surfaces.

The discharge through the liquid in all cases gave a continuous spectrum and some bright lines traceable to the electrodes, while the rays which we suppose to have been emitted by the molecules of the liquid were less conspicuous. It seems not unlikely, therefore, that the continuous spectrum was due to the particles thrown off the electrodes.

Liquid Oxygen.

When both electrodes were immersed in liquid oxygen boiling at atmospheric pressure, and therefore at about -180°C. , and the distance between the electrodes about one millimetre or less, the spectrum of the spark, without jar, was chiefly a continuous one, brightest in the yellowish-green but extending for some distance both on the red and on the blue side. The absorption-bands of oxygen were conspicuous on this bright background. A few bright lines also were seen, of which the most prominent were three in the green and yellowish-green, with the approximate wave-lengths 505, 533, and 547. These lines were not much brighter than the continuous spectrum. Glimpses of other lines were seen, but too faint and intermittent to be measured. Of these lines, that with wave-length about 533 is no doubt due to oxygen, for it is described as a triple line of the discharge in vacuous oxygen tubes by Piazzzi Smyth, and as a double line by Schuster. The other two lines appear to be lines of platinum, 5059 and two lines 5475, 5478, according to Thalén.

The introduction of a Leyden jar into the circuit increased the brilliance both of the continuous spectrum and of the lines, or of some of them, and brought out some additional lines; but the intermittent character of the sparks made it almost impossible to measure the places of any of the lines.

When the discharge from a Wimshurst machine was used instead of that from the coil, only a continuous spectrum, with the usual oxygen absorptions, was seen. No bright lines could be detected on the continuous spectrum.

By keeping only the lower electrode (the convex disk) immersed in the liquid, so that the spark passed partly through the liquid and partly through the gas immediately above it, the discharge took place more easily, and the continuous spectrum became, relatively to the lines, less bright. Without the jar, however, the spectrum had generally the same character as before. The three lines above mentioned were still the most conspicuous bright lines. On putting the jar into the circuit, however, many more bright lines came out. The well-known orange line of oxygen, $\lambda 6171$, appeared expanded into a band with its sharper edge on the more refrangible side at a wave-length of about 615, and fading towards the red but traceable as far as $\lambda 618$. Schuster and

Piazzì Smyth give a compound line at about wave-length $\lambda 6156$; and it is possible that this band may represent this compound line. It will be noticed that, as to the shading, it follows the character of A and B, but with the dispersion we used it was not possible to resolve it into lines. Probably, under the circumstances, the lines of which we may suppose the band composed would be so much expanded as to overlap one another. Besides this band, blue lines were conspicuous at wave-lengths about 435, 441, 459, 465, 470, all corresponding to known lines of oxygen. The green line of platinum at wave-length about 530 came out brightly, as well as platinum lines at about $\lambda 583$ and $\lambda 580$. Another line, less bright, appeared at wave-length about 557, and at times a second line near it at about 555. These have not been described as oxygen lines by other observers, but they fall within one of the green bands described by Schuster as seen in the negative glow in a vacuous oxygen tube.

We next proceeded to exhaust the gas above the liquid in the vessel until the pressure was reduced to about 1 centim. of mercury. The liquid, of course, boiled away fast until the temperature had fallen to something like $-200^{\circ}\text{C}.$; and the gas at the reduced pressure offered comparatively little resistance to the passage of the discharge.

So long as both electrodes were immersed in the liquid, the reduction of pressure and of temperature did not make any marked difference in the appearance of the spectrum. But as the liquid evaporated and only the lower electrode was immersed, so that the discharge was partly through the gas, the continuous spectrum was much weakened, and two bright green bands came out extending from about $\lambda 521$ to $\lambda 531$, and from about $\lambda 553$ to $\lambda 561$. This was without a jar in the circuit. The bands were nearly uniformly bright with both edges diffuse. They were much better seen when both electrodes were out of the liquid, and were brightest in the glow which surrounded the poles. They were equally well seen in the glow about both poles, and equally well when the electrodes were cold and when they were hot, even red-hot. There was a third much fainter band in the orange a little less refrangible than the D lines of sodium. There is no doubt that these bands are the same as have been described by Schuster in the negative glow in a vacuous oxygen-tube.

When a jar was put in the circuit, these bands disappeared or nearly so. While one electrode remained in the liquid, a good many bright lines came out on putting the jar into the circuit. One of these was a line at wave-length about 557, the same as previously seen, nearly in the middle of one of the green bands. In fact, it seemed to replace the band when the jar was put into the circuit. It was not, however, so permanently seen as some of the other lines. Only a few of these other lines were measured. One appeared to be an oxygen line at about $\lambda 544$; a pair at about $\lambda 566$ may

have been air-lines as the oxygen usually contains a little air. Another was a platinum line about $\lambda 455$.

The line above mentioned, $\lambda 557$, appears to be of some interest because it falls very near the place of the auroral line, and the conditions under which it is produced resemble, in regard to the low temperature, and to some extent in regard to the pressure, those in which Auroras are produced. The place of this line was measured several times, but the circumstances of these experiments were not very favourable for exact measurements. The measure which we marked as the best gave a wave-length for the line 5572, but other measures gave figures between that and 5578. It seems, therefore, not improbable that this line may be identical with the auroral line, of which the exact wave-length cannot even now be said to be quite certainly determined, but which has probably the value 5571.

The identity of the line we have observed with the auroral line cannot be said to be proved as yet. Further observation is needed, and we hope to carry our experiments further. The broad green bands do not seem to be connected with a low temperature, but were produced by the discharge without a jar; this line was, so far as we observed, only produced when one electrode was immersed in the liquid, and therefore cold, and when a jar was in circuit.

The passage of the discharge through the liquid produced much ozone. Not only was the smell of ozone very strong, but the liquid took the indigo tint, deeper than the blue of ordinary oxygen, which is characteristic of ozone. On one occasion, after the sparks had been passed through the liquid for a short time, an explosion ensued which shattered the vessel. We can assign no cause for this, unless it were an explosion of ozone.

Liquid Air.

The effects of a discharge through liquid air were very similar to those produced with liquid oxygen, so long as the pressure was that of the atmosphere, and no jar was in circuit. There was the same continuous spectrum. When a jar was used a much larger number of lines, generally resembling the ordinary air-lines, were seen but not measured. When the pressure was reduced, the usual banded spectrum of nitrogen was seen, and was strong relatively to the spectrum of oxygen. As the liquid evaporated, and thereby lost more nitrogen than oxygen, the two green bands due to oxygen appeared to become stronger actually as well as relatively to the nitrogen bands.

In this case the discharge produced oxides of nitrogen, which were detected in the residual gas when the air had all evaporated.

Liquid Nitrogen.

We next tried liquid nitrogen. At the pressure of the atmosphere, both electrodes in the liquid, and no jar, the spectrum was continuous with three bright lines in the green and yellowish-green, generally resembling the three lines seen in liquid oxygen. On taking measures of their wave-lengths it was found that they were platinum lines, the same as had been seen in oxygen at wave-lengths about 505, 530, and 547. The oxygen line at 533 was not seen. Besides these three lines, a faint very diffuse line was observed at about $\lambda 501$, and glimpses of blue bands of the usual banded spectrum of nitrogen. When only one electrode was immersed in the liquid, the line at about $\lambda 501$ was more distinct. We have no doubt that this represents the strong double line of nitrogen in that position. When the jar was in the circuit, the spectrum was a series of bright lines similar to those given by gaseous nitrogen at atmospheric pressure.

When the gas above the liquid was pumped out until the pressure fell to about 1 centim. of mercury, one or both electrodes being immersed, and no jar used, the band-spectrum of nitrogen appeared. On putting on the jar this was replaced mainly by the line-spectrum.

Spectrum of the Spark in Water.

For the sake of comparison we next observed the spectrum of the spark between platinum electrodes in distilled water at the ordinary temperature and pressure. When no jar was used the spectrum was continuous, with the red line (C) of hydrogen conspicuous, and the F line just visible, and glimpses of the three platinum lines in the green and yellowish-green. When the jar was put into the circuit the hydrogen lines became very diffuse, but the platinum lines came out much more distinctly, and the readings proved their identity. There were no lines which we could identify with oxygen lines.

The water became quite brown with the particles thrown off the platinum wires used as electrodes.

ON THE REFRACTION AND DISPERSION OF LIQUID OXYGEN,
AND THE ABSORPTION SPECTRUM OF LIQUID AIR

[*Philosophical Magazine*, Ser. 5, Vol. XL (1895), pp. 268 sqq.]

IN August 1892 we published in this Magazine (*supra*, p. 412) a measure of the refractive index of liquid oxygen at its boiling-point for the yellow sodium rays, made by means of a prism. In the following year (*supra*, p. 421) we published a measure of the same quantity made by a different method. For the reasons stated, we could only obtain measures more or less approximate to the truth. Since then we have made several attempts, but hitherto in vain, to make hollow prisms with vacuous jackets, in which the liquid oxygen could be kept in a tranquil state while the observations were going on. We have also attempted unsuccessfully other methods of taking the measures.

The chief difficulties which we encountered in making our former measures arose from the irregularities and striations of the glass vessels, and from the continual ebullition of the liquid oxygen. These difficulties have now been to a great extent obviated. We have come back to the method we used in 1893, which we then described as the method of MM. Terquem and Trannin, but which had previously been suggested by Prof. E. Wiedemann (*Archives de Genève*, li, p. 340, 1874). However, for the cylindrical vessel before used we substituted a globular vessel having the inside of its vacuous jacket silvered all over except a narrow vertical strip about 4 millim. wide, which was left unsilvered to allow of the passage of light. This vessel was used, exactly as the cylindrical vessel had been used in the former experiments, as a lens by which an image of a source of light was thrown on to the slit of a spectroscope. The pair of glass plates, separated by a thin stratum of air and fixed to a rod which was the prolongation of the vertical axis of a theodolite, were arranged at about the centre of the globe. The oxygen in the globe was very tranquil, and the silvering cut off all light which did not pass nearly centrally through the globe. The result was that the light of the rays observed was cut off, when the glass plates were turned through the proper angle, much more sharply than before, and the measures are so much the more trustworthy.

We found the spark between cadmium electrodes a convenient source of light, both because the rays are bright, and because they are dispersed through a considerable range in the visible spectrum, and it was possible to watch their extinction one after another as the glass plates were slowly turned. Even with this arrangement, the extinction of the rays when liquid oxygen was in the globe was not quite so sharp as when the experiment was made with alcohol. This was probably due to the scattered light from the bubbles in the oxygen, and was more troublesome in regard to the brighter rays.

We obtained as the mean of several observations for the blue ray of cadmium, $\lambda 4416$, $\mu = 1.2249$; for the red ray, $\lambda 6438$, $\mu = 1.2211$; for the green ray of thallium, $\lambda 535$, $\mu = 1.2219$. Also by using a flame we obtained for the red ray of lithium, $\lambda 6705$, $\mu = 1.2210$, and for the yellow rays of sodium, $\lambda 5892$, $\mu = 1.2214$.

The last figure is less than we had found in 1892 by the prism method, which was 1.2236, and still less than that found in 1893, which was 1.226. It is also less than that recently found by Olszewski and Witrowski (*Bull. de l'Acad. de Cracovie*, July, 1894, p. 246), which was between 1.2222 and 1.2235. The values we have now found for the refractive indices corresponding to the red ray of lithium and the green ray of thallium are also less than those found by Olszewski and Witrowski, which were about 1.2213 and 1.2235 respectively. We think, however, that our measures for the red and blue rays of cadmium are better than those made for the thallium and sodium rays.

These give for the mean green nearly $\mu 1.222$, and, taking the density of oxygen at its boiling-point as 1.137, the refraction-constant by Gladstone's formula becomes $\frac{\mu - 1}{d} = 0.1953$, and by Lorenz's formula, $\frac{\mu^2 - 1}{(\mu^2 + 2)d} = 0.1242$.

Taking Regnault's value for the density of oxygen gas at 0° C. and 76 centim., viz. 0.00143, and Mascart's value for the mean refractive index, viz. 1.000271, we find for gaseous oxygen the refraction-constant

$$\frac{\mu - 1}{d} = 0.18947$$

and
$$\frac{\mu^2 - 1}{(\mu^2 + 2)d} = 0.12631.$$

It will be seen that this last is nearly equal to the refraction-constant as above determined for the liquid.

In Mascart's paper "Sur la Refraction des Gaz" (*Annales Scientifiques de l'Ecole Normale*, 1877, pp. 9 sqq.) some observations on the Dispersion of Oxygen and other Gases were given, which enable a comparison to be made between this property in the gaseous and liquid states. Taking Cauchy's formula

$$n - 1 = a \left(1 + \frac{b}{\lambda^2} \right),$$

then

$$\frac{n' - n}{n + 1} = b \frac{\frac{1}{\lambda'^2} - \frac{1}{\lambda^2}}{1 + \frac{b}{\lambda^2}}.$$

From this b is calculated by Mascart, and is called the Coefficient of Dispersion. The blue and red cadmium lines represent the extreme difference of wave-lengths employed. They gave for the Constant of Dispersion for oxygen gas the maximum and minimum values 0.0078 and 0.0049, and a mean value 0.0064. Taking the values for the liquid state given above, the value of b becomes 0.0064. It seems possible, therefore, that the Dispersion Constant in the liquid state is identical with that of the gas.

In a recent conversation with M. Cornu about the absorption-spectrum of liquid oxygen, he suggested that it would be interesting to ascertain whether the diffuse absorption-bands were equally well developed when the increased density of the oxygen was produced by reduction of temperature at atmospheric pressure as when the gas was compressed at higher temperatures.

M. Janssen has found that the intensity of these diffuse bands increases as the square of the density of the oxygen, and has recently confirmed this (*Comptes Rendus*, June 17, 1895, p. 1306) by observations of the solar spectrum in the desert of Sahara. This law, as we have already pointed out (*supra*, p. 387), seems to indicate that these particular bands are due either to complex molecules generated by condensation, or to the encounters between molecules of ordinary mass which are more frequent when their free path is diminished.

To answer M. Cornu's question, we obtained liquid air directly from the atmosphere by the cold due to the rapid evaporation of liquid oxygen under reduced pressure. The method and apparatus have already been described by Professor Dewar (*Proc. Roy. Inst.*, Vol. xiv, p. 7).

The absorption of this liquid air in a thickness of 1.9 centim. was then directly compared with that of liquid oxygen in a thickness of 0.4 centim. The light which had passed through the latter was, by means of a reflecting prism, brought into the field of view of the spectroscope at the same time with that which had passed through the liquid air. The positions of the lamps were then adjusted so that the brightness of the spectra in those parts where there were no absorption-bands was equal in the two spectra. Under these circumstances, it was seen that the absorption-bands were very much more strongly developed by 0.4 centim. of liquid oxygen than by five times that thickness of liquid air.

The vessels containing the liquids being open, the liquid air gradually evaporated; and as the boiling-point of nitrogen is lower than that of oxygen, the former evaporated more quickly, and the residual liquid contained

a larger and larger percentage of oxygen. As this happened the absorption-bands became more intense, until they exceeded in strength those of the thinner stratum of liquid oxygen.

Another sample of air liquefied as before was rapidly mixed with an equal volume of liquid oxygen, and the absorption of this liquid compared, as before, with that of liquid oxygen. It was seen that the absorption of 2.4 centim. of the mixture was much greater than that of 0.4 centim. of liquid oxygen. The density of the oxygen in the mixture was in fact three times that of the oxygen in pure liquid air, and by Janssen's law the absorption should have been increased ninefold. Our observations accord with this so far as they go. Also these observations agree well with the theory of the continuity between the gaseous and liquid states. It must be borne in mind that air boils at a lower temperature than oxygen, so that the two liquids compared were not at the same temperature by some ten degrees. Now if the diffuse absorption-bands of oxygen are produced by the molecules during their encounters with each other in the gaseous and in the liquid states, it might well be supposed that they would be profoundly modified when the oxygen assumed the solid state. Hitherto oxygen has not, when pure, been solidified, but liquid air is readily brought to the solid state by rapid evaporation under reduced pressure (Dewar, *Proc. Roy. Inst.*, Vol. xiv, p. 393). Whether the solid in this case is homogeneous or only a magma of solid nitrogen mixed with liquid oxygen might be questioned*, but at all events it must contain oxygen at the lowest temperature that can practically be reached. We therefore tried whether we could detect any difference between the absorptions of solid and liquid air. There was no difference that we could detect in the character of the absorptions, and not much in their intensities.

In order to test further the effect of temperature, we compared the absorption of a thickness of 3 centim. of liquid oxygen boiling under about 1 centim. pressure with that of a like thickness of the liquid boiling at atmospheric pressure. With the colder liquid the bands in the orange and yellow were sensibly widened, mainly on the more refrangible side, the faint band in the green was plainly darker, and the band in the blue appeared somewhat stronger. The difference between the temperatures of the two liquids may have been about 17°C ., which does not appear to be a great difference; but then it is nearly one-fifth of the absolute temperature of the warmer liquid. The increased density of oxygen at -200°C ., according to Janssen's law, if extended to the liquid state, should make the absorption greater by about 20 per cent. as compared with that at its boiling-point.

* I have observed that solid air when placed in a strong magnetic field has the oxygen sucked out of it towards the poles, so that there seems little doubt that the solid air is only a magma of solid nitrogen mixed with liquid oxygen.—J. D.

ON THE FLAME-SPECTRUM OF MERCURY, AND ITS BEARING ON THE DISTRIBUTION OF ENERGY IN GASES

[*Proceedings of the Cambridge Philosophical Society*,
Vol. x. (1898), pp. 38 sq.]

HITHERTO, I believe, no flame-spectrum of mercury has been described, though that metal gives a spectrum of very brilliant rays when it is one of the electrodes of a spark discharge; and some years ago Prof. Dewar and I observed a very strong, diffuse, and easily reversed ray, with wave-length 2535·8, when mercury was introduced into the electric arc. Recently I have found that the same ray was produced by mercury heated in a flame of cyanogen burning in oxygen. As Prof. Dewar and I pointed out long ago, this flame is nearly the hottest known, on account of the endothermic character of cyanogen and the large amount of energy stored in the compound and liberated as heat when it is burnt. Besides the ultra-violet ray, λ 2535·8, I found another mercury ray developed in the cyanogen flame at wave-length 4358 in the indigo-blue.

The cyanogen was made by heating cyanide of mercury, and after passing through a spiral tube kept cool to condense the most of the mercury vapour, it was burnt at a platinum jet in the middle of a wider jet of oxygen. The spectrum was formed by a concave grating and photographed, and the wave-lengths of the rays determined by comparison with the iron spectrum.

The emission of these two rays in a flame where the stimulus appears to be only the high temperature, since mercury is not known to combine with either oxygen, carbon, or nitrogen at such a temperature, seems to be a fact of some theoretic interest. I cannot help regarding the production of spectra by an electric discharge as essentially a different process from the production by heat. The electric discharge may, not improbably, set up vibrations in the molecules directly, and the heat which attends the discharge, often only feeble, may be only a secondary phenomenon. At any rate a great many rays are given out by various elements in an electric discharge which have never been observed to result from mere heating. But the emission of light by hot mercury vapour is of interest in connexion with the fact that the ratio of the specific heats of mercury vapour, at constant pressure and constant volume, is almost exactly what it would be if none of the heat added were employed in

producing any vibratory motion, or other form of motion within the molecule. The spectrum emitted by mercury in the cyanogen flame proves that heat, at a sufficiently high temperature, is, in part, transformed into vibratory motion which affects the ether; and the true inference from the ratio of the specific heats appears to be, that, at the temperature at which this ratio was measured, the amount of heat converted into vibratory motion is very small compared with the amount which remains heat. What the temperature may be in the compressed gas during the passage of a sound-wave I do not know, but it cannot be very high.

In order to find an upper limit I had a tube, similar to those used for finding the velocity of sound in gases, filled, in the dark, with a mixture of hydrogen and chlorine in equal volumes, and then the tube was sounded by drawing it through the fingers covered with a resined glove. The sounding of the tube was repeated a good many times, but it did not, to any sensible degree, bring about a combination of the gases, for on opening the tube in a solution of soda the chlorine was absorbed and the hydrogen left in the original volume.

I think, then, that it must be allowed that, though at the temperature of the compressed gas in the sound-wave no sensible fraction of the heat is converted into vibratory motion in the molecules of mercury, this does not hold for higher temperatures.

If this be admitted we must abandon the hypothesis that, in gases, energy communicated to the molecules is distributed equally in all the degrees of freedom. I could never see any valid reason for this hypothesis, and many physicists have long ago repudiated it.

But there is another point. Some people see in the ratio of the specific heats of mercury vapour an argument for supposing that the molecules of that vapour, which are chemical atoms, are really the rigid spheres, which the old Epicurean philosophy suggested, and which have become familiar by their use as a working hypothesis for facilitating the mathematical calculations of the kinetic theory of gases. This hypothesis is untenable for other reasons besides the facts here adduced. Nevertheless it underlies the assumption that monatomic molecules are incapable of acquiring any vibratory or internal form of motion from energy communicated to them as heat, whence it has been concluded that every gas which is found to have 1.66, or thereabouts, for the ratio of its specific heats must be monatomic. It is possible that a chemically monatomic molecule may have, though it is not probable that it really has, a simpler constitution than a chemically complex molecule, and so may have not so many degrees of freedom as the latter, but still a plurality of degrees.

ON THE VARIATION OF INTENSITY OF THE ABSORPTION
BANDS OF DIFFERENT DIDYMIUM SALTS DISSOLVED IN
WATER, AND ITS BEARING ON THE IONIZATION THEORY
OF THE COLOUR OF SOLUTIONS OF SALTS

[*Proceedings of the Cambridge Philosophical Society*,
Vol. x. (1898), pp. 41 sqq.]

IN common with many others I have spent much time and trouble in trying to separate the elements of the Yttrium and Cerium groups of earths. Latterly my assistant, Mr Purvis, has for two or three years been fractionating some mixtures of these earths, and, though he has not succeeded in getting products spectroscopically pure, he has come across results which appeared to me worth following up. The investigation is yet far from complete, but a preliminary account of it may be of some interest.

The main facts are that while the absorption bands produced by solutions of the chloride and the nitrate have the same positions and general character in both salts, and the same intensities so long as the solutions are equivalent and moderately dilute, yet more concentrated equivalent solutions shew unequal variations in the intensities of the absorptions, some being stronger with the nitrate and others stronger with the chloride.

The mixture of earths used contained praseodymia and neodymia, samaria and some other earths, but was spectroscopically free from lanthana, though not from yttria. Some of the oxide was gently ignited, and equal quantities weighed out for solution in different acids so as to give solutions of equivalent strengths when diluted to equal volumes. The sulphate is so much less soluble than the nitrate and chloride, that equivalent solutions of these three salts could only be prepared in a rather dilute condition. In the case of the nitrate and chloride the solutions were evaporated to drive off all excess of acid and then redissolved in water. They were interposed between a lime-light and the slit of the spectroscope in tubes closed with quartz lenses at their ends so as to concentrate the transmitted light on the slit. The spectroscope had quartz objectives and calcite prisms. Also the spectra to be compared were always photographed in succession on the same plate, so

that inequalities in the development, as well as in the intensity of the light used, might be as far as possible avoided.

Equivalent solutions of the sulphate, nitrate, and chloride gave absorptions which were indistinguishable from each other. This is in accordance with the theory which has been worked out by Ostwald, that dilute solutions of salts which have one, and the same, coloured ion, with various colourless ions, all shew the same absorptions.

The absorptions by a thickness of 6 inches of each of a series of equivalent solutions of the chloride and nitrate were then photographed, the strength of the solutions being regularly graduated; and subsequently the absorptions by a thickness of 3 inches of the same series. The range of the spectrum photographed was from about a wave-length $\lambda 522$ to $\lambda 365$, and again, on a second set of plates, from about $\lambda 369$ to $\lambda 315$, *i.e.* nearly up to S of the solar spectrum.

The strongest solutions employed contained 21.6315 grms. of the oxide which, after conversion into nitrate, or chloride, was dissolved in 70 c.c. of water. The more dilute were prepared from this by successive dilutions to $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, ... to $\frac{1}{64}$ of the original strength.

Comparing the effects of the same thickness of solutions of the various degrees of dilution, we find in the region between $\lambda 522$ and $\lambda 365$:

1. That all the bands produced by the dilute solutions, both chloride and nitrate, are strengthened in the stronger solutions, and also widened, the more diffuse being most widened. The narrow, sharply defined, band about $\lambda 427$ retains its character, but is nevertheless sensibly widened.

2. The difference between the nitrate and chloride is that the light on the more refrangible side falls away in the spectrum of the chloride, from about $\lambda 420$, at a more rapid rate than in the spectrum of the nitrate. It is as if a broad, weak, absorption beginning from the more refrangible part, gradually extended down to the violet region, in the chloride, but not in the nitrate.

Also the light which gets through the chloride in the green seems a little less than that which gets through the nitrate, as if the chloride had a faint, broad, absorption band in the green which the nitrate had not.

If we accept the theory that the absorptions common to the salts in dilute solutions are due to their common ions, namely, the didymium and other metallic ions, then these broad absorptions, which appear to be added when a stronger solution of the chloride is employed, may be ascribed to the undecomposed chloride, or they may possibly be due to the chlor-ion. As they have not hitherto been observed to be produced by a solution of

hydrochloric acid, which must contain the chlor-ion, it is not probable that they are due to the chlor-ion.

Turning to the more refrangible section of the spectrum we find, with the weakest solutions ($\frac{1}{64}$ th the original strength), chloride and nitrate, four well-marked absorption bands between lines N and O of the solar spectrum, which may reasonably be ascribed to the didymium and other metallic ions. Light passing through the nitrate begins to fall away a little above O ($\lambda 344$), and thence onwards diminishes so rapidly that beyond about $\lambda 333$ nothing is seen in the photograph; while with the chloride light comes through quite to the edge of the plate ($\lambda 315$) but with diminishing intensity from $\lambda 345$ onwards.

With stronger solutions, $\frac{1}{16}$ the original strength, all the bands are expanded, and in the chloride a broad, diffuse, band shews itself between $\lambda 333$ and $\lambda 326$, and a faint, very diffuse band about $\lambda 338$. The nitrate lets hardly any light through beyond $\lambda 338$, and the light which gets through about $\lambda 344$ is very much weakened.

With still stronger solutions all light above $\lambda 360$, or thereabouts, is absorbed by the nitrate; also more and more is absorbed by the chloride, so that with the strongest solutions nothing at all is seen in the plates beyond $\lambda 370$.

In fact the fading of the light in the case of the chloride seems due to the gradual increase of a very wide and diffuse absorption extending farther and farther towards the less refrangible side.

In the case of the nitrate, there is a more marked absorption of a like kind by the dilute solutions, but it is not widened so much by the stronger solutions.

Throughout the series the absorption bands which are common to the chloride and nitrate are always, except in the most dilute solutions, a little stronger for the chloride than for the nitrate, the difference being more pronounced for stronger solutions. This may be accounted for by supposing a larger proportion of the chloride to be ionized than of the nitrate.

When the absorption produced by a thickness of three inches of a solution of the chloride is compared with that produced by a thickness of six inches of solution of half the strength, it appears that the bands in the blue, supposed to be due to the metallic ions, are stronger with the thickness of six inches of the weaker solution, whereas the effect of the broad diffuse absorption, affecting chiefly the most refrangible part of the spectrum, and supposed to be due to the un-ionized salt, is more marked with the smaller thickness of stronger solution. These effects are not very evident when the salt is nitrate; but that may be because the absorption ascribed to the un-ionized nitrate is both stronger and more sharply defined than that of the un-ionized chloride, so

that shades of variation cannot be so easily observed when the nitrate is used. As far as the chloride is concerned, these observations point to a relative increase in the proportion of the salt ionized as the solution is diluted.

Generally these observations tend to confirm the theory of Ostwald, but much more extended observations are needed, and some with other salts are already in progress. The effects of temperature will be taken in hand as soon as possible.

It is difficult to see how the ionization theory of solution can be tested spectroscopically in any other way, at least until we have learnt what the spectroscopic characters of the ions are. It is not possible, with our present knowledge, to predict the properties of ions, except so far as to say that, since the ions differ in their intrinsic energies from the elements of the salts ionized, it is almost certain that they will differ in their properties too.

Ostwald speaks of their being statically charged with electricity as a cause capable of changing their chemical and other properties; but statical charges seem to be affections of the field rather than of the charged bodies, and the intrinsic properties of charged substances are not found experimentally to be different from those of the same substances uncharged. On the other hand, what are called allotropic variations of a substance differ from one another in intrinsic energy, and the changes of energy which occur when the same element enters into the formation of two salts of different types, as for example ferrous and ferric chloride, are unequal. Hence we should expect the ferrous ion to differ in intrinsic energy from the ferric ion, and to differ also in properties, as we find solutions of ferrous and ferric salts to differ in colour. But though we may measure the changes of energy we cannot yet connect the amount of such change with any specific change of properties.

ON THE EFFECTS OF DILUTION, TEMPERATURE, AND OTHER
CIRCUMSTANCES, ON THE ABSORPTION SPECTRA OF
SOLUTIONS OF DIDYMIUM AND ERBIUM SALTS

[*Cambridge Philosophical Transactions*, Vol. XVIII. (1899), pp. 298 sqq.]

IN November 1898 I made a preliminary communication to the Society giving results of observations on the absorption spectra of aqueous solutions of salts of didymium in various degrees of dilution. Since then most of the observations have been repeated with improved apparatus, whereby several anomalies in the photographs have been removed, and a great many additional observations made, so that it will probably be best to make this communication quite independent of the preliminary one, and, at the risk of a little repetition, complete in itself so far as it goes.

APPARATUS.

The observations were made in part directly by the eye with an ordinary spectroscope, and partly by photography. On the former I rely only for the part of the spectrum below the indigo, on the latter for the more refrangible part. The spectroscope chiefly used for the former had two whole prisms of 60° and two half-prisms, all of white flint glass, telescopes with achromatic object glasses of 12 inches focal length, and eye-piece of very low magnifying power. It was useless to employ higher dispersion or magnification, because the absorption bands, even the sharpest of them which is that of didymium at about $\lambda 427$, are all diffuse, and higher dispersion or magnification renders some details invisible. In comparing by eye the spectra produced by two solutions, one was thrown in by reflexion in the usual way, and, after making the comparison, the positions of the solutions were interchanged and the observation repeated, in order to correct any error arising from a difference of intensity between the light entering directly and that coming in by reflexion.

For photography the spectrum was formed by one prism of 60° and two half-prisms, all of calcite, the object glasses of the telescopes were quartz lenses of 18.5 inches focal length for the sodium yellow light. The photographic plate was of course inclined to the axis of the telescope so that, as far

as the doubly refracting character of the calcite prisms allows, the image might be in tolerably good focus across the whole width of the plate, two and a half inches.

To concentrate the light, and make it, for the parts of the spectrum not subject to absorption, nearly uniform whatever the thickness of the absorbent stratum of liquid, a quartz lens of three inches focal length was fixed at that distance in front of the slit, and a similar lens fifteen inches further off, and three inches beyond the second lens was fixed a screen with a circular hole in it about one-eighth of an inch in diameter, and beyond that was of course the source of light. The centres of the hole in the screen and of the two lenses were aligned with the axis of the collimator. The distance between the lenses was fixed so as to allow of the interposition of the longest trough, used as a water bath for maintaining the temperature of the tubes containing the solutions. These troughs were of brass fitted with a plate of quartz at each end, and each had in it two V-shaped septa on which the tube with solution rested, and thereby took up at once its right position in the course of the pencil of light between the lenses. The tubes holding the solutions were of glass, fitted at the ends with quartz plates. These plates were held in position by outer brass plates with central circular perforations, connected by three wires passing along the outside of the tube and furnished with screw nuts by which the plates could be firmly pressed against the ends of the tube. The joint between the quartz plate and the end of the tube was made water-tight by a washer of thin rubber. The washers all had the same sized circular opening which determined the cross section of the pencil of rays falling on the slit. This seemingly complicated arrangement was adopted because it was necessary to have joints which would not be affected by a temperature of 100° , or by dilute acids, or by alcohol, and could be easily taken to pieces for cleaning the tube or plates.

Each tube had a branch on its upper side which was left open for the purpose of filling the tube, and to allow of expansion of the liquid when it was heated. Tubes of four lengths in geometrical progression, namely of 38 mm., 76 mm., 152.5 mm., and 305 mm., and a cell with quartz faces having an interval of 6.7 mm. between them, were used to hold the solutions; and for a few observations a cell of only 5 mm. thickness was used.

For observations on the effects of temperature, the trough containing the tube with solution was filled with water and a photograph of the spectrum taken at the temperature of the room; the trough was then heated by one or more gas lamps until the water boiled, the gas lamps were then lowered so as to maintain the bath 3 or 4 degrees below the boiling point, bubbles adhering to the quartz plates swept off with a feather, and when the whole appeared to be in a steady condition another photograph was taken. Unless the solution in the tube were a very dilute one there was not much trouble with

bubbles in the solution, but bubbles in the bath were very troublesome, and had to be removed because they impeded the passage of the light, and thereby affected the photograph. A similar effect is produced by convection currents of unequal density. These were pretty well avoided within the absorbent liquid, but could not be completely avoided in the water of the bath. The difference of temperature, and consequent difference of density, of the currents in the water was, however, small, and the thickness of water between the end of the tube and the quartz window of the trough also small, so that the currents were not of much consequence. Attempts to use temperatures below that of the room were abandoned because of the dew which settled on the quartz windows. Wetting the quartz with glycerol was no remedy, because the glycerol gravitated, destroyed the plane figure of the window, and dispersed some of the light. Very fair observations by eye of the effect of heat on a solution, not too dilute, were made by fixing two similar test tubes containing the solution, one in front of the slit and the other in front of the reflecting prism, and after adjusting their positions until the two spectra, seen simultaneously, were identical, heating up one of the test tubes by placing a lamp under it. For dilute solutions, requiring a greater thickness to give absorption bands of sufficient intensity, two of the tubes used for the photographs were employed, one of them being heated up in its water bath.

As a source of light a Welsbach incandescent gas lamp without chimney was chiefly used. This was placed 5 or 6 inches from the screen so that the network of the mantle was quite out of focus at the slit. It gave a good light up to a wave-length of $\lambda 370$, but beyond this point it would not produce a good photograph without an exposure too prolonged for the less refrangible part of the spectrum. For the region above $\lambda 360$ a lime-light was used.

Inasmuch as the bands observed are all more or less diffuse, and fade away gradually on either hand, any variations of the intensity of the source of light, of the sensitiveness of the photographic plates, or of the development of the image, tend to mask the effects of varying the composition, or the temperature, of the solutions; so that two photographs can be fairly compared, for the sake of determining these effects, only when they have been taken with the same light, on the same plate, with equal times of exposure, and have been developed together. This has been attended to throughout. The photographs to be compared with each other have always been taken in succession on the same plate, with no other change than the necessary shift of the plate and the substitution of one tube of liquid and its bath for another. The photographs taken thus in succession do very well for comparison of the intensities and other characters of the absorption bands, but cannot be depended on for the detection of a very small shift in the position of a band. That could be done if the two spectra to be compared were in

the field at the same time, one of them reflected in, but I have not attempted to photograph two spectra in this way, and have been content to detect alterations of wave-length, in the bands most easily visible, by the eye without photography.

THE SOLUTIONS EXPERIMENTED ON.

These have been chiefly those of salts of didymium and erbium. Most coloured salts have only very wide absorption bands which fade on either hand very gradually, so that it is extremely difficult, or even impossible, to recognise small changes in them. On the other hand, didymium and erbium salts have a great many absorption bands, of various degrees of sharpness and of intensity, and distributed through a wide range of the spectrum. No other salts seem so well adapted for my purpose. However, I made a number of observations on uranous chloride, but found it so prone to chemical change when in solution that I could not with certainty distinguish the effects of dilution, or of elevation of temperature, from those due to chemical change. The absorption spectra of salts of cobalt have already been investigated by Dr Russell, though not exactly from my present point of view, and they are not as good for my purpose as the salts of the two metals to which I now confine myself.

Both series of salts had been purified as far as possible, by my assistant Mr Purvis, by a long series of fractional precipitations. The didymium was spectroscopically free from lanthanum, but it had not been found possible to get it, or the erbium, so free from yttrium*. No attempt was made to separate the neodymium from the praseodymium, and there is no method at present known for separating the various metals of which ordinary erbium is supposed to be a mixture. Indeed for my purpose there would be no advantage in doing so; though for a quantitative estimation of the concentration of absorbent material in the solutions it was important to get rid of an admixture of unabsorbent salt. In order to obtain solutions of the salts of different acids in equivalent concentration the metal was precipitated as

* Lanthanum and yttrium cannot be recognised by any absorption bands, but when induction sparks are taken from solutions of their salts, each gives a very characteristic channelled spectrum, by which it is easily recognised in a solution containing one per cent., or even less, of the salt. The yttrium channellings are in the orange, the brightest of those of lanthanum in the citron and green, and both fade towards the red. Thalén in his paper (1874) on the Spectra of Yttrium and Erbium, and of Didymium and Lanthanum, gives the wave-lengths of the sharp, more refrangible edges of the yttrium channellings, one set beginning at λ 6131 and the other at λ 5970.5. He does not give those due to lanthanum. These I find to consist of three sets in the green and citron of which the brightest begin at λ 5599 and λ 5380 respectively, and the third at λ 5173. There is another weaker set in the orange beginning at λ 5865, and two sets in the indigo beginning at λ 4419 and λ 4370 respectively. My measures were not made with any large dispersion and the last figure of the measured wave-length may not be quite correct, but near enough for recognition of the channellings which are easily seen with a small spectroscope, especially the two first mentioned.

oxalate, washed, dried, and ignited in air until it was reduced to oxide. Weighed quantities of this oxide were dissolved in the several acids, and, in the case of nitric and hydrochloric acids, the solutions evaporated and excess of acid driven off. The residual salts were then dissolved in measured quantities of water. The most concentrated solutions of didymium employed contained, respectively, of the nitrate, 611.1 grams to the litre, and of the chloride the equivalent quantity, namely 462.9 grams of anhydrous chloride*. These each contain 1.862 gram-molecules of the salt per litre, and as the specific gravity of the solution of chloride is 8.295, it appears to contain one molecule of the chloride to between 27 and 28 molecules of water.

Didymium sulphate is rather sparingly soluble in water, so that the most concentrated solution of it employed contained only 58.11 grams of it per litre. For comparison with it, the strongest nitrate, or chloride, had to be diluted to 9.16 times its bulk.

Of erbium the most concentrated solutions used contained, respectively, of the nitrate 935.2 grams to the litre, of the chloride 726.6 grams. These each contain 2.67 gram-molecules of the salt per litre. The solution of the nitrate was a saturated one at a temperature of about 15°.

Less concentrated solutions were also prepared and used, containing, respectively, 566 grams of nitrate of erbium, and 440 grams of the chloride to the litre, or about 1.61 molecules in grams to the litre.

The more dilute solutions were obtained from these by taking measured quantities of them and diluting up to the required volume. In fact the most concentrated of these solutions were the stock solutions, and may conveniently be described as of strength No. 1. Half strength will mean such a solution diluted until the bulk was doubled, one-quarter strength will mean No. 1 diluted until its bulk was quadrupled, and so on.

Other salts and solvents were employed, and will be described when the experiments upon them are described. The solutions of nitrate and chloride above mentioned were, as a rule, the standards of concentration.

THE ABSORPTION BANDS OBSERVED.

The didymium absorption bands, of which I have taken notice in this investigation, are as follows:

A band in the red at about λ 679.

A weak band at about λ 623.

A rather weak band at about λ 596.

* The (crystalline) didymium chloride in this solution was dissolved in just about twice its weight of water; the equivalent solution of nitrate had still less water.

The strong group extending from about λ 590 to λ 570, consisting of a number of bands overlapping one another.

A rather weak band at about λ 531.

A strong group of about four, more or less overlapping, bands, extending from about λ 528 to λ 520.

A less strong group of two diffuse bands with the centre about λ 510.

A well-marked triplet at about λ 483, 476 and 469, of which that in the middle is decidedly weaker than the other two.

A broad weak band, with its centre at about λ 462, and extending nearly down to the most refrangible band of the triplet above mentioned.

A very broad band with its centre about λ 444.

A very weak band „ „ „ λ 433.

A strong, narrow, sharply-defined band at about λ 427.

A very weak diffuse band with its centre about λ 418.

A still weaker one with its centre about λ 415.

Another weak diffuse band at about λ 406.

A very broad strong band with its centre about λ 403.

A very weak diffuse band at about λ 391.

A diffuse band at about λ 380.

Another, wider, at about λ 375.

A weaker band at about λ 364.

Four, nearly equally distributed between λ 358 and λ 350, which in all but the weakest solutions run into one broad band extending beyond the above-mentioned limits.

A weak diffuse band at about λ 338.

And a broad diffuse band with its centre about λ 329.

These bands appear all to belong to didymium, or to the metals associated under that name, for though they may be modified in character, and even in position, by the solvent and other circumstances, they all disappear in the absence of didymium, and they retain so much the same general character under all circumstances, that it is reasonable to infer that they have the same primary cause. A reference to plate No. 17, page 470, on which are reproduced photographs of the spectra of didymium chloride in solution in water, in alcohol, and in alcohol charged with hydrochloric acid, will make my meaning evident.

The erbium absorption bands of which I have taken notice in this investigation are as follows:

A group of four bands in the red, of which the most refrangible but one is much the strongest and has a wave-length about λ 653.

A group of four, of which the more refrangible two are much stronger than the others, lying between λ 536 and λ 549.

A weak band at about λ 527.

A very strong one at about λ 523.

A weaker one at about λ 520.

A rather broad band, strongest on its more refrangible side and fading towards the less refrangible, with its strongest part at about λ 491.

A strong band at about λ 488.

A weaker one at about λ 486.

A broad but weak band with its centre about λ 472.

A sharp but weak band at about λ 467.

A broad, diffuse band with centre about λ 454, reaching almost up to a stronger, and narrower, band at about λ 449. These two are merged into one with concentrated solutions.

A weak band at about λ 441.

A narrow one at about λ 422.

A weak one at about λ 418.

A broad band, fading on its less refrangible side, and extending from about λ 415 nearly down to the band at λ 418.

A pair of nearly equal bands, rather strong, at about λ 404 and λ 407.

A very faint but broad band extending from about λ 396 to λ 402.

A well-marked, rather narrow band at about λ 379,

And a weaker one almost touching it on the more refrangible side, which becomes merged with it, and with a still weaker diffuse band at about λ 377, in solutions a little stronger.

A weak diffuse band with centre about λ 367.

A strong band at about λ 365, accompanied by

One rather less strong at about λ 363, which become merged together when the solution is rather stronger.

A band rather weaker than the last at about λ 357, and

A broad weaker band with centre at about λ 353, which soon merges in the former when the solution is a little increased in strength.

All these bands more refrangible than λ 404, expand rapidly and become very diffuse at the edges as the solution is more concentrated, so that they may easily be confounded with a diffuse continuous absorption which extends

from the ultra-violet down the spectrum as the solution becomes more concentrated; but they are common to the nitrate and chloride, and may be seen with a solution of the former when with an equivalent solution of chloride the advancing continuous absorption has obliterated them. The superposition of this continuous absorption, even when it is very weak and scarcely otherwise perceptible, strengthens and widens the bands.

EFFECTS OF DILUTION.

For observing the effects of dilution, equal volumes of the stock solutions were diluted to 2, 4, 8, 45.5, 61 or 91 times their original volumes, and the absorptions produced by thicknesses of these solutions proportional to their dilutions observed and photographed.

In the spectra of either didymium or erbium chloride, starting with solutions half the strongest, or less strong, in thickness of 38 mm., I can find no change with dilution, when accompanied by proportional increase of thickness, below λ 390: see plate 1, page 458. With the strongest solution in a thickness of 38 mm. a diffuse absorption creeps down from the most refrangible end of the spectrum, as may be seen in the uppermost spectrum in each of the plates 8 and 9. Above λ 375, or thereabouts, it seems to cut off all the light, but the diffuse edge extends with the strongest didymium chloride as low as λ 415, making the absorption bands look wider and stronger by its superposition. On comparing with the eye the spectrum of a thickness of 5 mm. of the strongest solution of didymium chloride, with that of 305 mm. of the same solution diluted to 61 times its volume, both spectra being in the field of view at the same time, I could detect no difference between them.

Again, photographing the spectrum of a thickness of 6.7 mm. of the strongest didymium chloride, and that of 305 mm. of the same solution diluted to 45.5 times its original bulk, I can find no difference between the photographs, which take in a range from about λ 350 to λ 600. Plate 5 is a reproduction of these photographs. This identity of the spectra extends to the intensities, even of the weakest bands that I can see, as well as to the positions of the bands, and even to the apparent extinction of the diffuse absorption which is produced by a greater thickness of the strongest solution at the ultra-violet end.

Also erbium chloride of half the strongest concentration, in a thickness of 5 mm., gives a spectrum which cannot be distinguished by my eye from that given by 305 mm. of a solution 61 times as dilute. And photographs of the spectrum of the same solution, half the strongest, in a thickness of 6.7 mm., are identical with those of 305 mm. of the same solution diluted to 45.5 times its bulk, below a wave-length of about λ 380. Plate 7 is a reproduction of these photographs. The triple band at about λ 378 comes out more strongly

with the stronger solution, but I am not sure whether this is not an effect due to the superposition of the diffuse absorption creeping down from the more refrangible end. In the region above λ 355, a thickness of 152 mm. of a very dilute solution of didymium chloride transmits a sensible amount of light as high as λ 315 (the highest part of the spectrum included in my photographs) but with a gradually fading intensity from about λ 348 upwards. And this diffuse absorption creeps further down as the solution is stronger until with a solution half the strongest, in the same thickness, it reaches λ 360. Didymium bromide produces a similar diffuse absorption which extends lower than in the case of the chloride; and didymium sulphate shews something of the same kind.

This diffuse absorption, which creeps far down the spectrum of the most concentrated solutions of the chlorides of both didymium and erbium, seems to belong to a different category from that to which the other bands belong. For not only is it diminished by dilution when the thickness of the stratum is proportioned to the dilution, but it is diminished by diminishing the thickness of the strong solution, without diluting it, at a greater rate than the other bands are diminished, for some of the ultra-violet bands which are quite obscured by it when the liquid is 38 mm. thick are visible in the photographs when the same liquid is only 6.7 mm. thick. The obvious suggestion is that it is due in some way to the common element, the chlorine. Most chlorides, however, produce no such absorption. I have tried solutions of calcium, zinc, and aluminium chloride, respectively, and found them, in a thickness of 305 mm., very nearly as transparent as water for the range of the spectrum included in my photographs, namely below λ 355. One chloride I have found, when in a concentrated solution, to behave like the didymium and erbium chlorides, and that is hydrochloric acid, whether it be dissolved in water or in alcohol. Plate 10, page 464, is a reproduction of a photograph of the spectra of solutions in alcohol, and in water, of hydrochloric acid, in several thicknesses, and in proportional degrees of dilution, along with one of distilled water for comparison.

The increasing extent of the absorption with increasing concentration of the solution is manifest; and the most probable cause is some action between the molecules of acid during their encounters, for it seems to depend on the number of molecules of acid (or salt) and on their concentration, jointly. We cannot ascribe the absorption to the chlorine ion, because the number of chlorine ions increases with dilution; but the close correspondence of the effects strongly suggests a common cause in all the solutions which give those effects. It should be observed that the percentage of chlorine in the concentrated solution of the acid used in these experiments bore to that in the most concentrated solution of didymium chloride the ratio of about 39 to 14.5. The extent, down the spectrum, of the absorption now in question, is

increased, as might be expected, by adding hydrochloric acid to the didymium solution, and also by raising the temperature as described below. In connexion with this it may be remarked that concentrated neutral solutions of didymium, and erbium, chloride lose the clean pink tint, by transmitted light, of their dilute solutions, and take up more of an orange hue, due of course to the diminution of the rays at the blue end of the spectrum.

As above stated I have been unable to obtain a solution of didymium sulphate so concentrated as my strongest solution of chloride; but using the solution containing 58.11 grams to the litre, and diluting it to twice, four times, and eight times its bulk, I could find no change in the absorption spectrum produced by it when the thickness of the absorbent liquid was proportioned to the dilution, either when directly viewed or when photographed. See plate 2, which however does not include any part of the spectrum below the green. Nor could I detect any difference between the spectrum of the sulphate and that of an equivalent solution of the chloride.

Didymium nitrate in four dilutions, beginning with the strongest in thickness of 38 mm., and ending with one-eighth strength in thickness of 305 mm., gave spectra which could not be distinguished from each other, in the range photographed. See plate 9, page 463, where the spectra are those of equivalent solutions of the chloride and nitrate alternately, beginning with 38 mm. of the strongest solution of chloride, next the equivalent nitrate, then 76 mm. of the solutions of half strength, 152 mm. of one-quarter strength, and ending with 305 mm. of the two solutions of one-eighth strength. This appearance of identity is brought about, however, by the diffuseness and strength of the absorptions by which the details of the groups of bands are obliterated. When the spectra of the same solutions in much less thickness are examined, it is seen that the bands of the stronger solutions of nitrate are more diffuse, or wider, than the bands produced by equivalent solutions of the chloride. The weak bands look washed out, the strong are wider than the corresponding bands of the chloride, and in the strong groups the component bands are merged together. By increasing dilution the several bands contract themselves and become better defined, until, with solutions of $\frac{1}{32}$ strength, I am unable to see any difference between the bands of the nitrate, chloride, and sulphate in equivalent solutions. In the stronger solutions the weak bands look weaker as well as broader with nitrate than with chloride, the strong bands are broader but look no weaker; but I think that when an absorption is very strong the eye does not perceive, nor a photographic plate always record, a small difference of intensity. There is no indication of an increase of intensity of the bands of the nitrate by dilution with corresponding increase of thickness. There are, on the other hand, indications of a shift of the positions of greatest absorption in the bands in the yellow and green, which remind me of the much greater shift of these bands by the use of alcohol and other solvents instead of water.

Comparing small thicknesses (5 mm.) of solutions, the big band in the yellow expands with the nitrate beyond that produced by the equivalent solution of chloride, especially on the less refrangible side. Of the four strong components of this band the least refrangible seems, with the nitrate, to be displaced a little towards the red, and a less strong diffuse band extends still further beyond the corresponding band of the chloride on the red side. The less refrangible of the two strong groups in the green, which for the chloride consists of two nearly equal strong bands separated by a narrow chink of light, and of a fainter very diffuse absorption extending some way down towards the red, has for the nitrate the less refrangible strong band widened out by diffusion, some way beyond its limit for the chloride on the red side, and the more refrangible is weaker with the nitrate. The more refrangible group in the green appears with the nitrate as a single band narrower than the two given by the chloride, and the middle band of the triplet in the blue is more diffuse with the nitrate.

The apparent shift above mentioned may be an effect of the overlapping of the diffuse bands, and though a real shift does not seem to me improbable, it is not in this case sufficiently decided to found an argument upon.

Plate 4 reproduces the spectra of 6·7 mm. of the strongest solution of didymium nitrate and of 305 mm. of the same solution diluted to 45·5 times its bulk. The bands of the strong solution are more diffuse and look somewhat washed out, notably the narrow band about λ 427, and the middle band of the triplet in the blue; and the strong group in the yellow extends further towards the red and has the appearance of being stronger with the strong solution than with the dilute.

Erbium nitrate behaves quite in the same way as didymium nitrate in regard to the greater diffuseness of its bands with strong solutions, and their gradual contraction and growing sharpness as the solution is diluted, until they come to be identical with those of the chloride. This is better seen in the photographs of the erbium spectra than in those of the didymium: see plate No. 3.

In plate 6 the spectrum of 6·7 mm. of solution containing 467 grams of erbium nitrate to the litre is contrasted with that of 305 mm. of the same solution diluted to 45·5 times its bulk. The greater diffuseness of the bands of the upper spectrum, which is that of the strong solution, and apparently greater intensity of the ultra-violet band on the right will be noticed. It may be compared with the corresponding plate No. 7 for the chloride, in which however the lower spectrum is that of the stronger solution. Plate 8 contrasts the spectra of equivalent solutions of erbium chloride and nitrate, in four degrees of dilution, the uppermost spectrum being that of the strongest chloride. The greater diffuseness of the bands of the nitrate can be seen, and

the gradual approximation to identity in the spectra of the two solutions as they become more dilute. It is the counterpart for erbium of plate 9.

The nitrates, as well as the chlorides of both metals, shew a general absorption creeping down from the most refrangible end of the spectrum with increased concentration of the solutions; but though similar in the two salts, that given by the nitrates is not identical with that of the chlorides. Its edge is not so diffuse, but cuts off the spectrum more sharply than that of the chloride; and in the strongest solutions it does not extend so far down the spectrum as that of the chloride. On the other hand with the weak solutions of didymium it extends lower than that of the chloride. With a solution of didymium nitrate of $\frac{1}{64}$ strength in thickness of 152 mm. all light above $\lambda 333$ seems to be absorbed, while with the chloride light gets through beyond $\lambda 315$; and the strongest solution of the nitrate in a thickness of 38 mm. does not entirely cut off the light below $\lambda 360$, while the equivalent solution of chloride cuts it off much lower.

There are here four facts to deal with:

1. The identity of the spectra of the different salts of the same metal in the dilute condition.
2. The constancy of this spectrum in the case of chloride and sulphate in different dilutions so long as the thickness of absorbent is proportional to the dilution, a constancy holding good in the chlorides for a great range of concentration.
3. The modification, for I take it to be only a modification, of this spectrum in the case of the nitrate, by some cause which has increasing effect with increasing concentration.
4. The absorptions at the most refrangible end of the spectrum, which are somewhat different for different salts of the same metal, and diminish with increased dilution.

The first of these facts is certainly strongly suggestive of the interpretation put on it by Ostwald, that the spectrum common to all the salts of the same metal is due to the metallic ions. Against this the second fact militates, for the ionization is supposed to increase with dilution, and the absorptions by the ions should increase in intensity by dilution when the total quantity of salt, dissociated and undissociated, through which the light passes remains the same. The third fact points to some cause, affecting the diffuseness of the bands, which is more effective in concentrated solutions. This cause may be encounters between the molecules of the salt, or of its products in solution, which would be more frequent in more concentrated solutions.

Ionization should be increased by heating the solutions, and diminished by the addition of acid. I proceed to describe what I have observed of the effects of heating and of acidification on the absorption spectra.

EFFECTS OF TEMPERATURE ON THE SPECTRA.

The rise of temperature which could be employed was, as described above, only from the temperature of the room, about 20° , to a few degrees below the boiling point of the water bath, or to about 97° . This rise of temperature produced the same kind of effect on all those absorption bands which are common to all the salts of the same metal, whether it be didymium or erbium, and that effect was to render them more diffuse, to spread them out, make their limits less definite, and in the case of weak bands make them appear weaker. The effect of heat was also the same in kind on dilute as on concentrated solutions. Heat also caused the broad diffuse absorption at the most refrangible end to extend itself downwards in a marked degree. Plates 11, 12 and 13, pages 465 to 467, are reproductions of photographs of the spectra of three salts, in various degrees of dilution, cold and hot. It will be noticed that the absorption bands are not increased in intensity by heat, but from the greater diffusion they seem weaker, except the very strong bands which are so intense that they bear diffusion without letting enough light through to affect the plate. The creeping down with the higher temperature of a diffuse absorption from the most refrangible end is seen in all, and with the nitrate and sulphate seems to be independent of the concentration, while with the chloride it is barely noticeable with any but the most concentrated solution. In the last exposure with the sulphate the light is a little weaker throughout. The solution was the weakest and in the longest tube, and therefore most likely to be troubled with bubbles on the inner faces of the terminal quartz plates which could not be removed. I have no doubt this general weakening of the light was due to this cause. A general weakening of the light has the effect of making the absorption bands appear stronger. This appearance is deceptive; for the examination of a great many photographs, as well as direct observations of the spectra by eye, have led me to the conclusion that the effect of heat is to diffuse and not to strengthen the absorption bands which are ascribed to the metals. On the other hand it looks as if the diffuse absorption at the most refrangible end, which certainly creeps down lower with hot solutions, were strengthened as well as diffused, for in the region above that included in the plates, the limit of complete extinction of photographic effect is considerably lower with the hot than with the cold solutions.

On the whole the effects of heat on the spectrum afford no confirmation of the supposition that the absorptions are due to an increase of the number of ions; but rather suggest that they may be due to the increased energy of the motions of translation of the molecules, causing more frequent encounters.

EFFECTS OF ACIDIFYING THE SOLUTIONS.

The solutions compared with a view to ascertain these effects had in every case equal quantities of the metallic component per litre, but while one was neutral the other had twice as much of its acid component as the first; and they were usually compared in various degrees of dilution and in thicknesses proportional thereto. With didymium salts, chloride and nitrate, the acid made very little difference in the bands, as will be seen by examination of plate 16, page 469, which gives the spectra of four solutions of the chloride, two neutral and two acid. The creeping down of the absorption at the most refrangible end is, however, very evident in the most concentrated solution of acidified chloride; and some diffusion of some of the bands of the nitrate by the addition of the acid is just traceable in photographs of some of the weaker bands of the more concentrated solution. The increased diffusion of the bands of the nitrate by the addition of nitric acid can be easily seen directly by eye, using weak solutions in no great thickness. The addition of acid also produces a slight shift of the places of greatest absorption in the strong groups in the yellow and green. Whether this is due only to the expansion, and consequent overlapping, of the several bands in these groups, or whether there is a real shift, I have not been able to satisfy myself; but the general appearance resembles the changes produced in those bands by the use of different solvents which are described below, and it is very likely that similar causes are at work in the two cases. Nothing of this kind can be seen on the addition of hydrochloric acid to the chloride.

With erbium nitrate the addition of acid produces more marked effects: see plate 15, page 469. All the bands which are more diffuse with the neutral nitrate than with the equivalent chloride solution, are still more diffuse with the acid nitrate; and the effect regularly diminishes as the solution is made more dilute. There is however no indication that there is any weakening of the intensity of the bands by the presence of acid, but rather a strengthening of them.

With the chloride, on the other hand, there seems to be no more difference between the absorptions of the neutral and acid solutions than there is between the corresponding solutions of didymium chloride. Comparing the spectra by eye, I can see no appreciable difference between the acid and neutral solutions of equal thickness and equal erbium concentration. Plate 14, page 468, gives a reproduction of photographs of the absorptions of two pairs of equivalent neutral and acid solutions of erbium chloride, the upper pair being those of the strongest solution. The creeping down of the continuous absorption with the acid solution is visible in both pairs of spectra, but more evident with the stronger solution, where it sensibly affects the apparent intensity and breadth of the broad band at about λ 451. The second pair of spectra on this plate were taken with solutions made by diluting those used

for the first pair of spectra until their volumes were three times as great as before, and they were put into tubes four times as long as those used for the first pair. There is no indication of any weakening of the absorptions by the addition of acid.

The absence of any diminution of intensity either of the didymium or erbium bands by the addition of acid, taken in conjunction with the fact that rise of temperature does not increase their intensity, goes a long way to negative the supposition that these bands are produced by the metallic ions; and the facts recorded in the preceding pages rather suggest that the metallic bands are the outcome of chemical interactions between molecules of the salt with each other and with those of the solvent, while the general absorption at the most refrangible end, which is evidently of a different class and resembles the absorptions of glass and many other substances which absorb the more rapid vibrations but are transparent to waves of less oscillation-frequency, may perhaps be due to encounters of molecules without chemical change. The effects on the spectrum when different solvents are used may throw some light on this question. Accordingly I made some experiments with didymium salts in various solvents.

EFFECTS OF DIFFERENT SOLVENTS.

Didymium chloride solution evaporated at 100° retains some water, and seems to have the composition of the crystalline salt. Dried at a higher temperature it may be had anhydrous, but in that state appears to be quite insoluble in alcohol. Dried at 100° it dissolves with tolerable facility in absolute ethyl-alcohol, and in glycerol, but will not dissolve in benzene. The alcoholic solution deposits beautiful pink crystals on evaporation. The absorption spectrum of this solution shews the same bands as an aqueous solution, but they are somewhat modified. They are more diffuse so that the weaker bands look as if they were washed out, and the positions of maximum absorption are all moved towards the less refrangible side, and the diffuse absorption at the most refrangible end extends lower down the spectrum than with an aqueous solution of equal concentration. The general relation between the spectra of the two solutions will be seen on comparing photographs (1) and (2) of plate 17, page 470, of which the former is given by the aqueous, the latter by the alcoholic solution. The shift of the bands towards the red is visible in the photographs, but as the plate had to be shifted between the exposures, no reliance can be placed on the appearance of a shift in such photographs, when the amount of displacement of the bands is small. This defect is, however, met by direct eye-observations, with the two spectra in the field of view at the same time. In this way it is seen that all the bands that are visible are shifted towards the red, but are by no means all equally shifted. At the same time the strong groups of bands in the yellow and

green have, by the action of the alcohol, undergone a modification of their general appearance which simulates the addition of some new bands; but by examining solutions of different concentrations I have satisfied myself that no new bands make their appearance, but the simulation of them is due to the widening and unequal shift of the bands, whereby their overlapping, and the consequent relative positions of the maxima of absorption, are modified. The modifications are such as we may reasonably ascribe to the influence of the bulky colloid molecules of the alcohol, amongst which the vibrating absorbent molecules move and from which they can hardly ever get free, loading them but loading them unequally, and on the whole degrading the rates of their vibratory motions.

A very remarkable, and by far the most excessive, modification of the bands that I have observed, is produced by passing dry hydrochloric acid into the alcoholic solution. The third photograph of plate 17 shews the effect. The colour of the solution is changed by the acid from pink to bluish green, and the reason of this is obvious from the photograph. The molecules seem so loaded as to be nearly incapable of taking up the more rapid vibrations corresponding to the bands in the indigo and blue, while they seem to absorb more strongly those of slower rate in the yellow and citron. At the same time these are more degraded than by alcohol alone, and the group in the yellow so spread out that some of the components are distinctly separated. Of course the acid makes the solvent a complicated mixture, including ethyl-chloride and water as well as the unaltered components.

The modifications of the spectrum by glycerol are of the same character as those produced by alcohol. The bands are generally shifted towards the red, and are more diffuse, but otherwise not much modified. Plate 18, page 470, shews the spectrum of the glycerol solution below that of an aqueous solution of didymium nitrate of nearly, but not exactly, equal concentration. Observed directly by eye it is seen that the band in the red at $\lambda 679$ is not sensibly affected, the group in the yellow, and the less refrangible of the two groups in the green, are distinctly shifted towards the red, but otherwise not affected in character; while the more refrangible group in the green is not sensibly shifted, but appears weakened by diffusion. The still more refrangible bands are all rendered more diffuse by glycerol, and are also degraded with the exception of the middle band of the triplet in the blue, which does not appear shifted, but of this I am not sure for the photographs shew a trace of a washed-out band about midway between the two extreme bands of the triplet in addition to the stronger band which is more refrangible. With glycerol the continuous diffuse absorption also creeps down the spectrum as with alcohol.

In order to observe the effect of a crystallizable solvent other than water, some didymium acetate was prepared and dissolved in glacial acetic acid, and

for comparison with it an aqueous solution of didymium nitrate was made of equal concentration. Plate 20, page 471, shews the photographs of their spectra. Comparing the absorptions directly by eye, the band in the red appeared stronger in the acetate and sensibly shifted to the less refrangible side, the feeble band in the orange also was shifted in the same direction, the strong group in the yellow considerably extended towards the red but its more refrangible edge not apparently shifted, doubtless because the widening of the bands compensated the shift which was visible in all the other bands of the acetate though they otherwise had the same general appearance as those of the nitrate. The shift and change of character produced by acetic acid was less than was produced by alcohol.

Didymium tartrate is very insoluble in water, but the compound produced by potassium hydrogen tartrate acting on didymium hydroxide dissolves in a solution of ammonia. The spectrum given by this solution is contrasted with that of an aqueous solution (not exactly of the same concentration) of didymium chloride in plate 21, page 472. With the exception of the group in the yellow, the less refrangible of the groups in the green, and the narrow band in the indigo, the bands seem all a good deal washed out. All the bands are shifted towards the red, and the *apparent* shift increases as the bands become more refrangible, but probably this appearance is the effect of the greater dispersion of the more refrangible rays.

I had no crystals of didymium salts sufficiently large to enable me to see how the diminished freedom of the molecules in the solid would modify the spectrum, but had a rod of fused borax coloured with didymium. This was made by mixing weighed quantities of didymium oxide and dried borax, fusing the mixture, and sucking the fused mass into a hot platinum tube. After cooling the rough ends were cut off and polished, and I was thus able to compare the spectrum given by a thickness of 25 mm. of this glass with that of an equivalent solution of didymium chloride. Photographs of these spectra are shewn in plate 19, page 471. They are somewhat marred by dust on the slit of the spectroscope, but this does not prevent a fair comparison. It will be seen that the modifications produced by the glass are on the whole similar in character to those produced by some of the liquid solvents. The strong group in the yellow is much expanded and the components of the group unequally shifted towards the red, the less refrangible of the groups in the green is shifted and its appearance modified for the same reason. The more refrangible bands are much washed out and their shifts appear very unequal. Nevertheless they appear to be still essentially the same bands modified as to their rates of vibration by the diminished freedom of the molecules producing them.

On a review of the whole series of observations I conclude that the characteristic absorptions of didymium compounds, namely those which are

common to dilute aqueous solutions, and are only modified by concentration, by heat, and by variations of the solvent, are due to molecules which are identical in all cases, though their vibrations are modified by their relations to other molecules surrounding them. The like conclusion holds for erbium compounds. It appears to me quite incredible that the atoms of didymium should retain in chemical combination so much individuality and freedom as to take up their own peculiar vibrations unaffected by the rest of the matter combined with them, as must be the case if we supposed the combined didymium *in the molecules* to give the common spectrum of all the salts in dilute solution. When I speak of atoms of didymium in the salts, I mean of course masses equal to the atoms of didymium metal, but having different energy, which means different internal motions, probably different structure, and different capabilities of vibration. No chemical compounds shew the absorptions which their separate elements exhibit. Sodium vapour, though monatomic, has a very strong absorbent power which is quite lost when it has parted with energy in combining with chlorine. Nevertheless the molecule of a chloride breaks up, in general, into masses equal to those of the atoms of its elements more easily than in any other way, and there is pretty good evidence that in encountering a molecule of water this also is sometimes broken up, and ultimately, if not immediately, new molecules of hydroxide and acid are formed, as well as, by a similar process, new molecules of the salt. In the interval between the rupture of a molecule and the recombination of its parts with each other, or with parts of other molecules, the parts have a certain freedom, and capability of vibrating, which they do not possess in combination. Now if we suppose the number of such parts as have the capability of taking up vibrations of frequency corresponding to the characteristic absorptions of didymium to be directly proportional to the concentration of the didymium salt and to the time of their freedom, the observed facts will be all in agreement with the hypothesis. Increased concentration, and increased temperature, will mean more frequent encounters amongst the molecules, and more frequent ruptures, but at the same time more frequent encounters of the parts and consequent shortening of their times of freedom. These effects will exactly compensate each other and leave the average number of absorbent parts of molecules constant under changes either of concentration or of temperature. The continuous absorption of the more rapid vibrations increasing with concentration and rise of temperature points to an action depending only on the number of encounters of the molecules of the salt with one another. It is not every encounter which is attended with disruption, and the continuous absorption may be due to molecules in encounter without rupture, but at all events it seems due to the condition of the molecules during encounter, but not to occur at the encounters of a molecule of salt with the very much less massive molecules of water. Encounters of a molecule of salt with a molecule of acid will in all probability cause

effects very similar to those of encounters between two molecules of salt, and this supposition is quite in agreement with the observed facts.

The time of complete freedom of a vibrating part of a molecule must be very short, but probably shorter when the complementary part is more massive, as in the case of a nitrate, than it is in the case of a chloride. But between complete freedom and complete incorporation in a chemical compound there is a considerable gradation, and the capacity of the part to vibrate at particular rates will have a corresponding gradation, and the part may moreover be frequently under the influence of molecules, or parts of molecules, with which it does not combine. This influence will probably be greater as the molecule exerting the influence is greater, whether more massive, or, as in the case of such colloids as alcohol, more voluminous. These considerations reconcile all the facts as to the spectra I have observed with the hypothesis I have made.

There are, however, other facts to be reconciled with that hypothesis. I mean the facts of ionization, of osmotic pressure and the correlative facts of the rise of boiling point, and fall of crystallizing point, of solutions. In regard to all these effects the freedom of the parts is the primary postulate, far more definitely so than in the case of vibrations such as my observations relate to. The laws I have tried to investigate appear to hold good up to the point of saturation of the solutions, which is not the case with the laws of osmotic pressure and of change of boiling and freezing points, which have been established for dilute solutions. Further, ionization implies a certain distribution of energy in the field, the ions are charged with electricity. That is not necessary for the absorption of light, which will depend, primarily at least, on the form of the internal energy of the vibrating mass, that is on its structure. That a redistribution of energy occurs at every rupture of a molecule seems certain, solution is attended with thermal effects and so is dilution, and it is only when equilibrium is reached, and as much change takes place in one direction as in the opposite, that the manifestation of such redistribution ceases. How much of the intrinsic energy of the molecules takes the form of heat and how much is retained in the field at the rupture of the molecules we do not know. It is however quite conceivable that the circumstances under which the rupture takes place may determine whether any, or how much, energy is retained by the field, that is whether any, or how many, of the ruptured parts become ions.

PLATES 1-21 illustrating the effects of Dilution, Temperature, and other circumstances, on the Absorption Spectra of solutions of Didymium and Erbium salts.

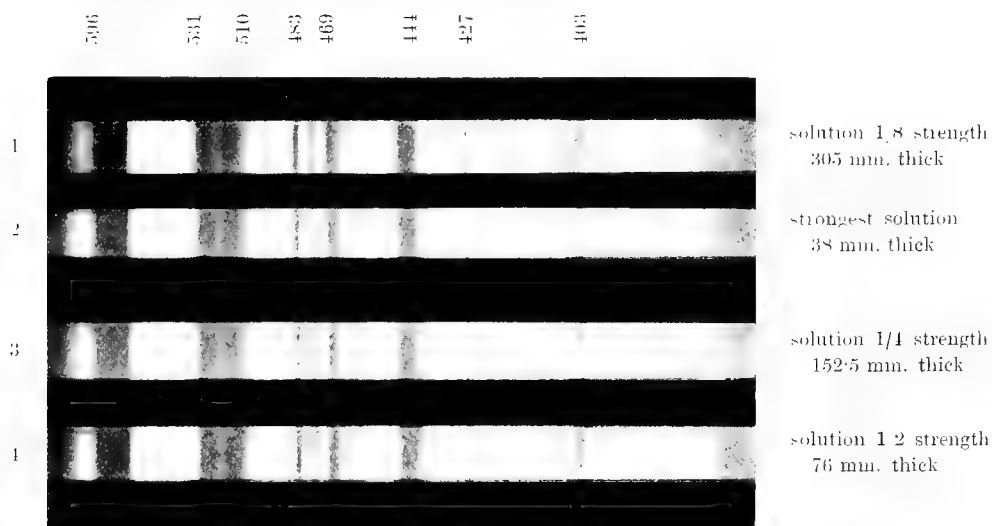
These plates are all reproductions, enlarged to double the size, of photographs of some of the spectra from which the conclusions in the text have been deduced. In the processes of enlargement and reproduction some of the fainter details visible in the original negatives have (perhaps unavoidably) been lost; but they present the salient features of the changes in the spectra produced by the variations of circumstance.

The references to these plates in the text applied to the original negatives and were printed before the reproductions were ready. The latter, being positives, are reversed, and in order that the references may be easily intelligible it has been necessary to place the red ends of the spectra on the left hand.

The figures at the top of each plate are the approximate wave-lengths of the bands in the spectra beneath them, and sufficiently indicate the range of the spectrum photographed.

PLATE 1.

Absorptions of solutions of didymium chloride in four degrees of dilution in thicknesses inversely as the dilutions. The most concentrated solution contained 140.7 grams per litre, and the absorbent thickness of this solution was 38 mm.



It will be noticed how very nearly identical these four spectra are. The original photograph shows a number of faint bands which have not come out in the reproduction. They are however as nearly identical in all four spectra as are the stronger bands here reproduced.

PLATE 2.

Absorptions of solution of didymium sulphate in four degrees of dilution

510 433 439 441 445 403 380 375



The diffuse bands at about $\lambda 380$, 375 and 364 are quite visible in the original photograph, but have nearly disappeared in the reproduction.

PLATE 3.

Absorptions by solution of erbium nitrate in four degrees of dilution, the strongest containing 566 grains of the salt to the litre.

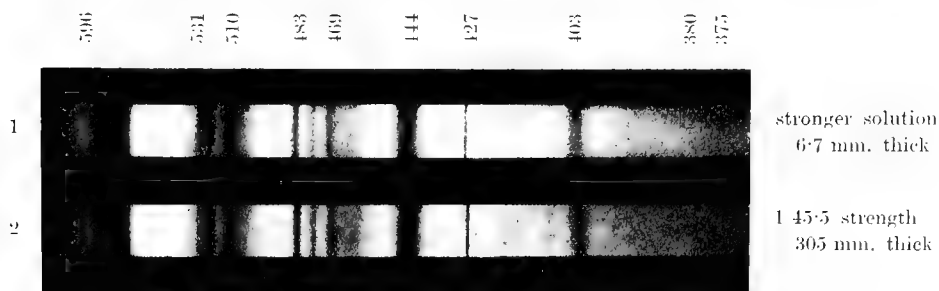
523 427 449 441 415 404 387 377 365



The increasing diffuseness of the bands with increased concentration of the solution is seen in this series: the weak band about $\lambda 441$ seeming to be washed out when the solution is concentrated while that about $\lambda 449$ is much broader and the details within it obliterated.

PLATE 4.

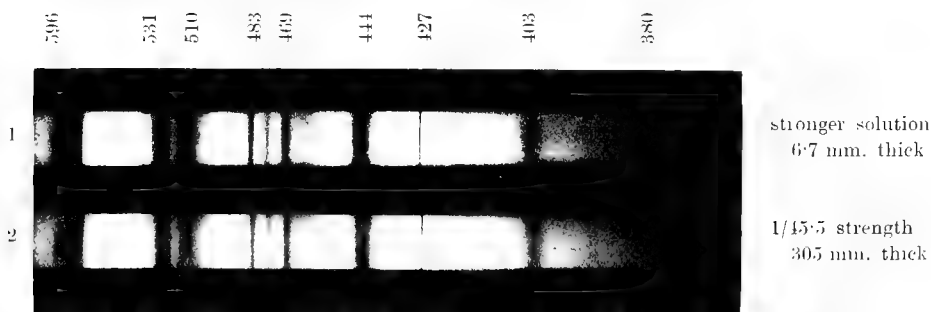
Absorptions by solutions of didymium nitrate, concentrated, and extremely dilute. The most concentrated had 611.1 grams of the salt per litre: the other was part of the same solution diluted to 45.5 times its bulk.



There is very little difference between these two spectra except that the band in the yellow is broader with the stronger solution, and those at $\lambda 476$ and $\lambda 427$ more washed out.

PLATE 5.

Absorptions by solutions of didymium chloride of concentrations equivalent to those of the nitrate used for plate 4: the stronger containing 462.9 grams of the chloride per litre.



There is no definite difference between these two spectra.

PLATE 6.

Absorptions of a solution of erbium nitrate containing 467.6 grams of the salt per litre, and of a solution made by diluting the former to 45.5 times its bulk.



The bands are more diffuse with the stronger solution, that at about $\lambda 377$ being decidedly broader. The band at about $\lambda 449$ is more distinctly seen in the original and is more diffuse with the stronger solution than with the weaker.

PLATE 7.

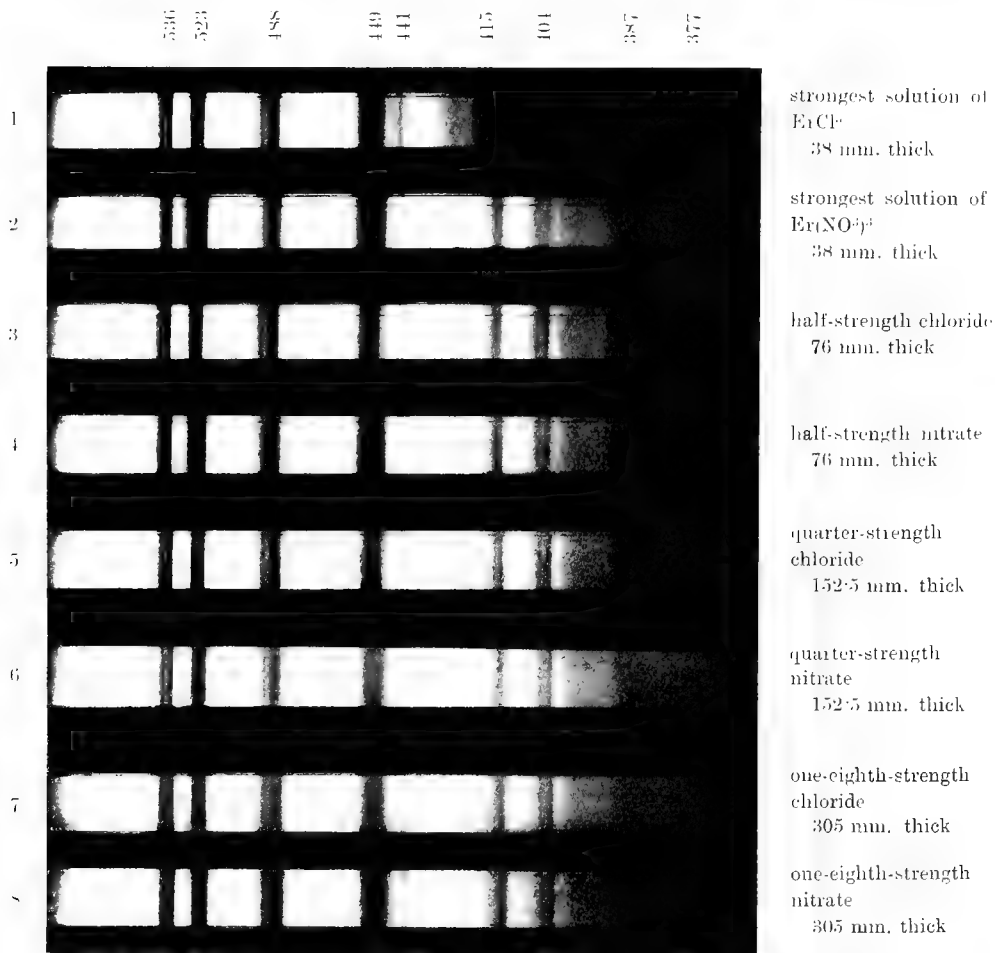
Absorptions by solutions of erbium chloride of concentrations equivalent to those of the nitrate used for plate 6; the stronger solution containing 363.3 grams of the salt per litre.



There is hardly any difference between these two spectra except that the band about $\lambda 377$ is rather stronger with the more concentrated than with the dilute solution, owing probably to the overlapping of the general diffuse absorption of the concentrated chloride at the more refrangible end. The fainter bands which are visible in the original photograph can hardly be traced in the reproduction.

PLATE 8.

Absorptions by solutions of erbium chloride and equivalent solutions of erbium nitrate, alternately: four degrees of concentration, the strongest having 726.6 grams of the anhydrous chloride to the litre, and the equivalent nitrate 935.2 grams to the litre.

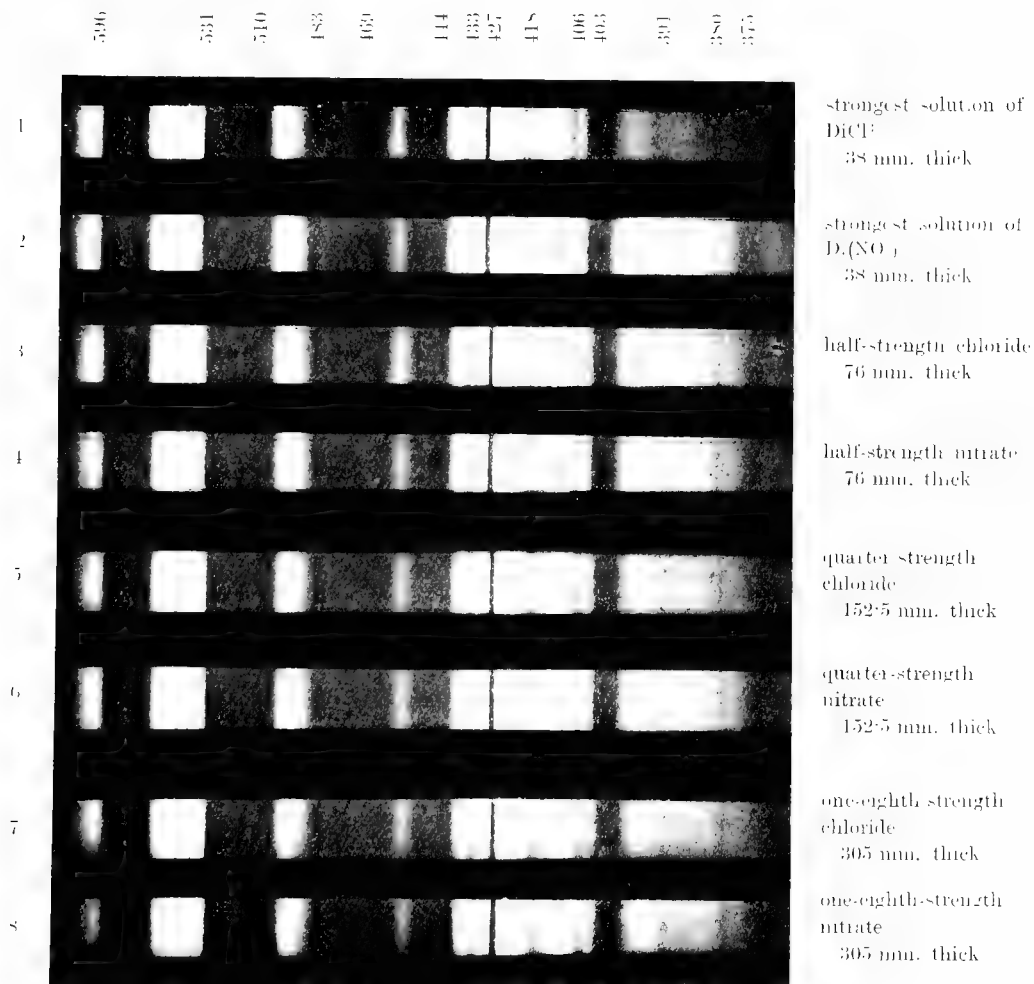


The greater diffuseness of the bands with the more concentrated solutions of the nitrate is evident, and so is the extension of the general absorption at the more refrangible end of the spectrum with the most concentrated solution of the chloride.

The difference between the absorptions by the chloride and nitrate diminishes with dilution and has almost, or quite, disappeared in the case of the weakest solutions.

PLATE 9.

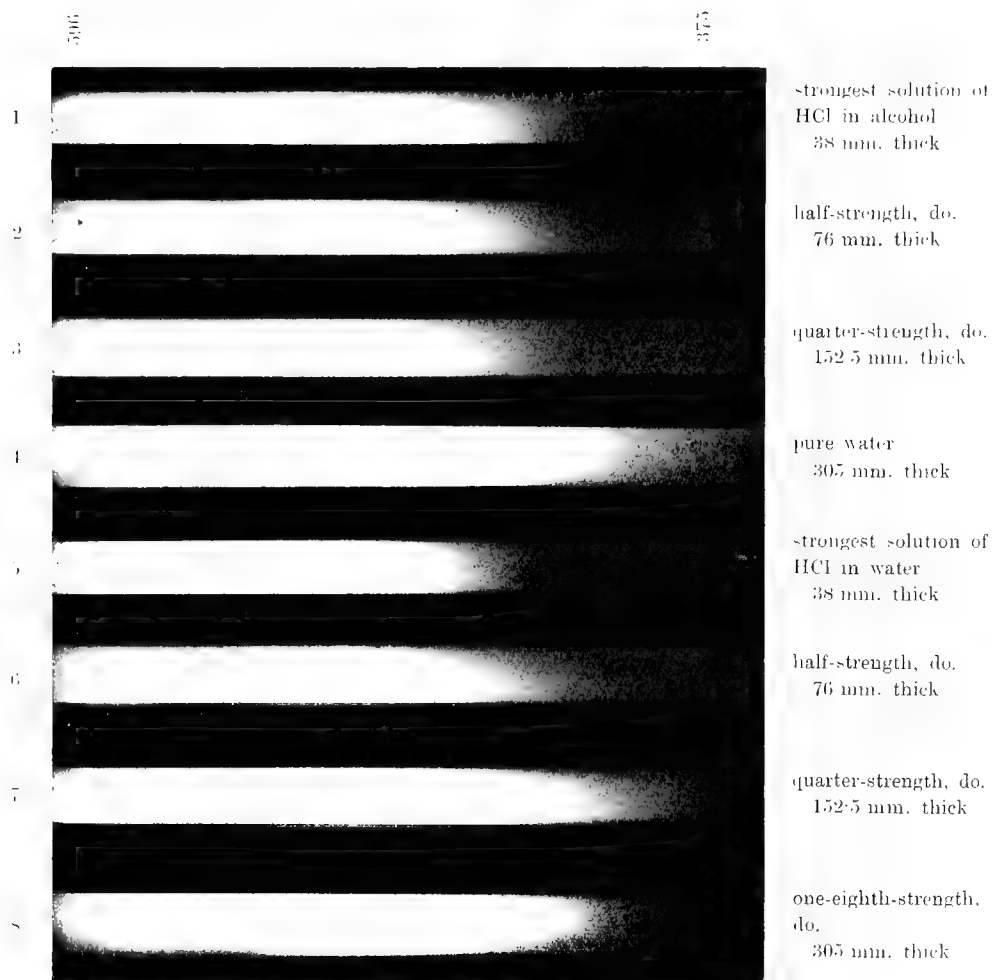
Absorptions by didymium chloride and nitrate, alternately, in equivalent solutions of four degrees of concentration, beginning with the strongest solution containing 462.9 grams of the anhydrous chloride to the litre, followed next with the equivalent solution containing 611.4 grams of nitrate to the litre.



The extension of the general absorption at the most refrangible end of the spectrum with the concentrated solution of chloride is evident in the uppermost figure. With such strong solutions as were used for these photographs other differences between the absorptions by chloride and nitrate can be seen only in the weaker bands such as those from λ 433 to λ 406. These are weakened by diffusion in the case of the nitrate, but there is very little difference between the absorptions by chloride and nitrate in the most dilute solutions.

PLATE 10.

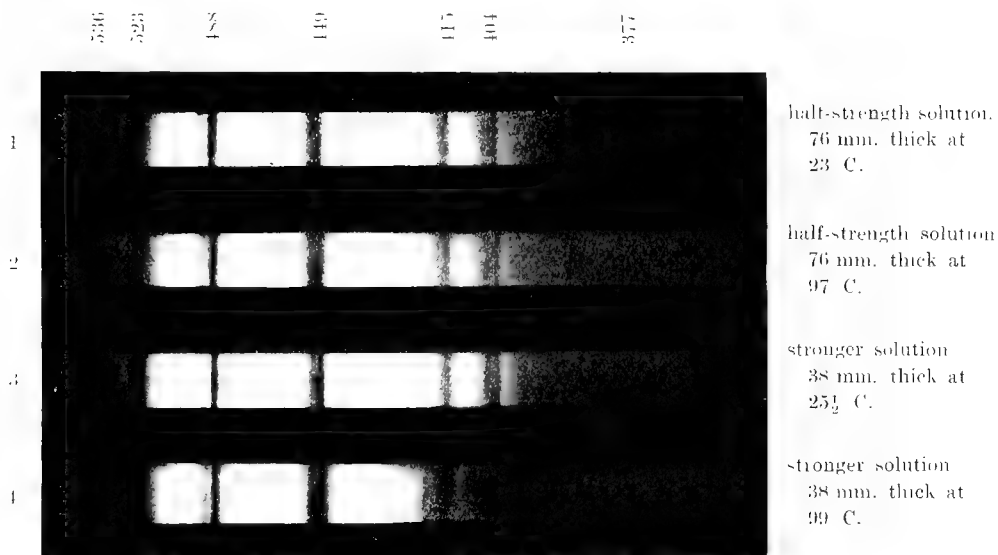
Absorption by solutions of hydrochloric acid in alcohol, and in water, compared with the absorption by pure water.



The effect of the hydrochloric acid at the more refrangible end is visible, and the diminution of the absorption with diminished concentration of the acid is seen in the aqueous solutions Nos. 5, 6, 7, while diminished concentration has little or no effect in the case of the alcoholic solutions Nos. 1, 2, 3.

PLATE II.

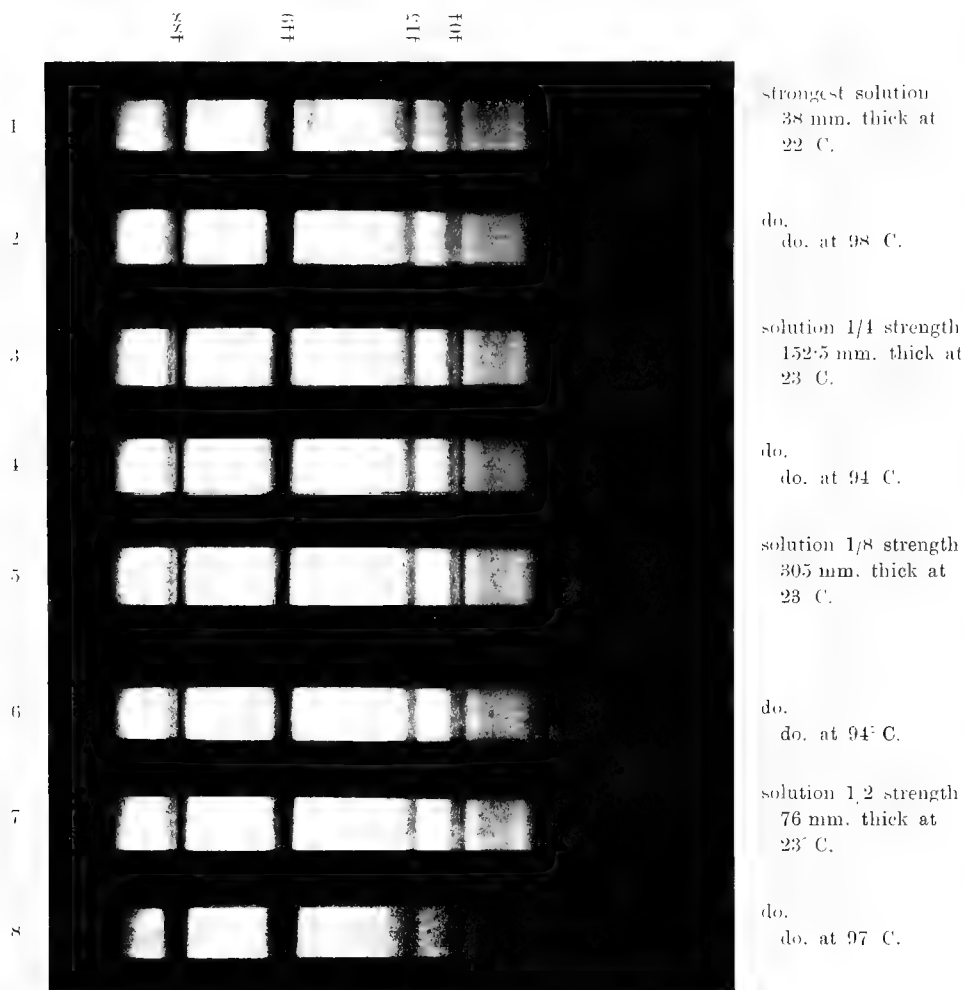
Absorptions by solution of erbium chloride, cold and hot alternately, in two degrees of concentration.



The extension of the general absorption at the more refrangible end of the spectrum by a rise of temperature is manifest in these photographs, and so is the greater diffuseness of the bands at about $\lambda 449$ and $\lambda 488$.

PLATE 12.

Absorptions by solutions of erbium nitrate, cold and hot alternately, in four degrees of dilution, in thicknesses inversely as the dilutions. The strongest solution had 566 grams of erbium nitrate per litre.

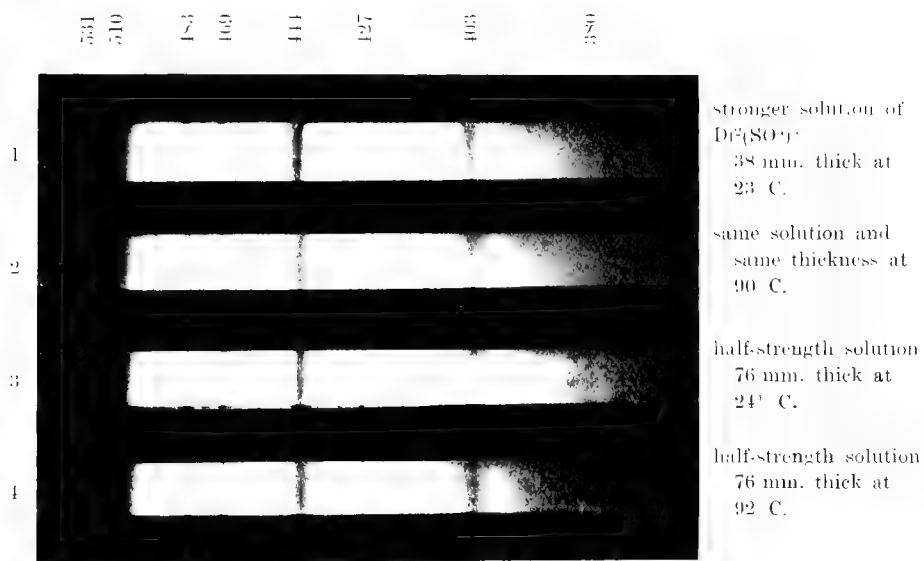


It will be noticed that the effect of heating the solution is in general to render the absorption bands more diffuse, and that it is the bands that increase in diffuseness with increasing concentration of the solution which are most affected by the rise of temperature.

The original photographs shew several fainter bands which have not come out in the reproduction, and also shew the lighter interspaces between the absorptions in the ultra-violet much more distinctly than the reproduction. Even in the reproduction these lighter interspaces in the ultra-violet are more distinct in the spectra of the cold solutions than in those of the hot solutions.

PLATE 13

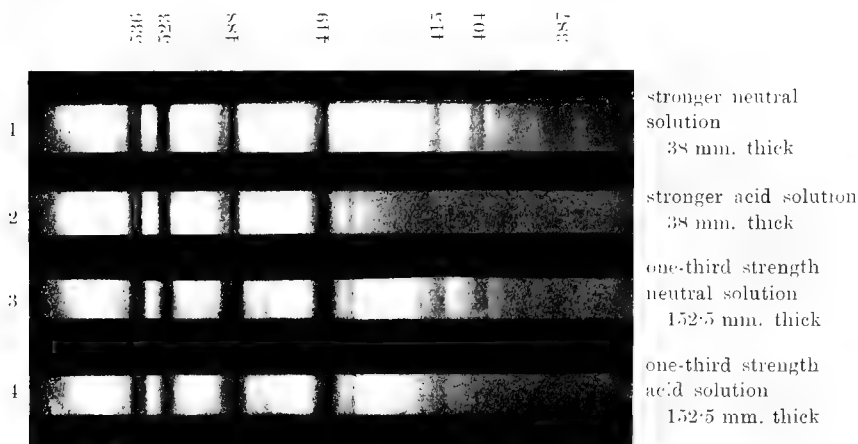
Absorptions by solution of didymium sulphate, cold and hot, in two degrees of concentration. The stronger solution was a saturated solution at 20° C.



The extension of the general absorption at the more refrangible end of the spectrum, and the increased diffuseness of the bands in the blue, by the rise of temperature is plainly seen in these photographs.

PLATE 14.

Absorptions by solution of erbium chloride, neutral and acid, in two degrees of concentration; the stronger neutral solution having 726.6 grams of the chloride to the litre, and the acid solution having besides an amount of hydrochloric acid equivalent to the amount of neutral salt.

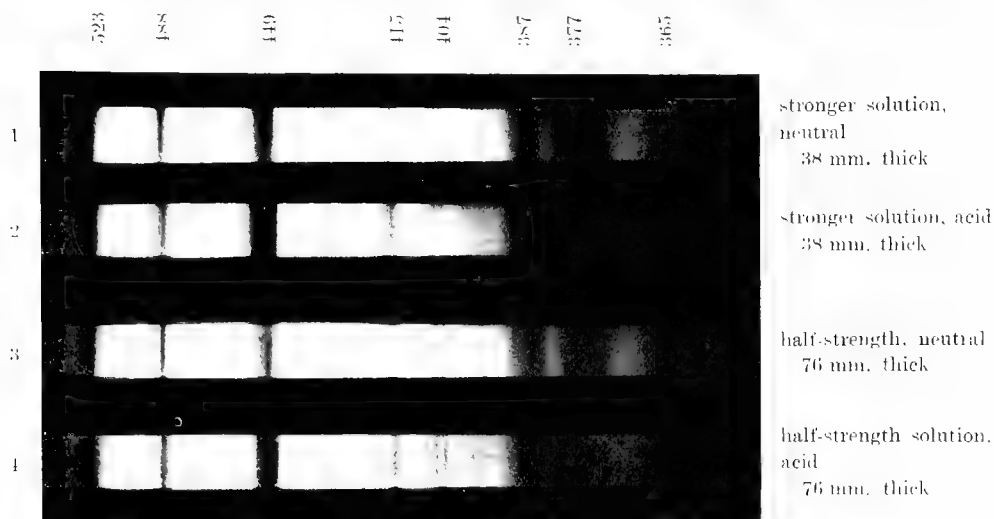


The thickness of the absorbent solutions is not proportional to the dilutions, so that the absorptions of figures 3 and 4 are produced by a quantity of salt one-third greater than that which gave figures 1 and 2, which makes the bands of 3 and 4 stronger.

The effect of the acid is chiefly to extend the general absorption at the more refrangible end of the spectrum.

PLATE 15.

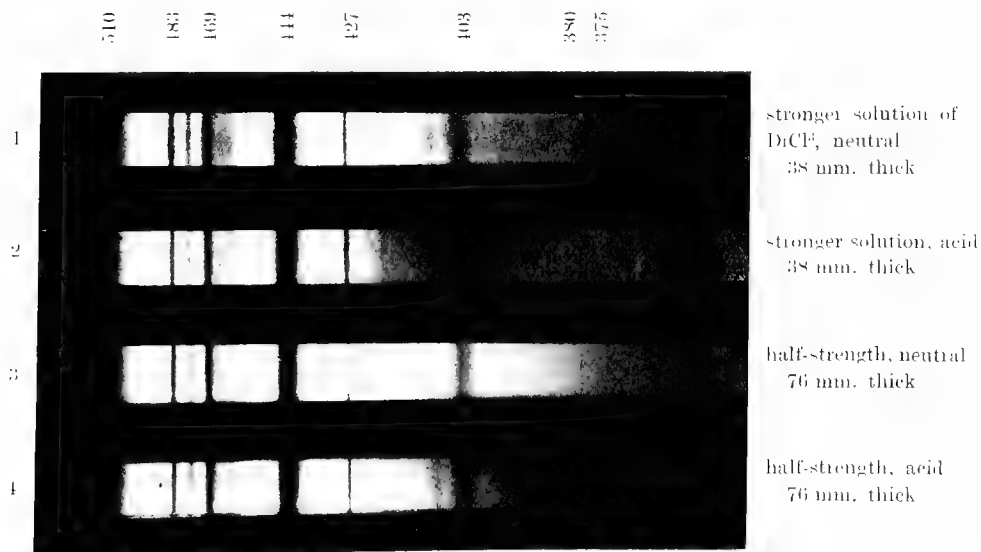
Absorptions by solutions of erbium nitrate, neutral and acid, in two degrees of concentration. The stronger neutral solution had 935.2 grams of the salt per litre, and the acid solution had in it besides as much nitric acid as was equivalent to the amount of neutral salt.



The effect of the acid in rendering the bands more diffuse is seen in these photographs, and in the extension of the general absorption at the more refrangible end of the second figure.

PLATE 16.

Absorptions by solutions of didymium chloride, neutral and acid, in two degrees of concentration: the acid solutions containing the same amount of didymium per litre as the neutral solutions but with hydrochloric acid in addition.



The chief effect of the acid is to extend the general absorption at the more refrangible end of the spectrum.

PLATE 17.

Absorptions by nearly equivalent solutions of didymium chloride in water, in alcohol, and in alcohol charged with hydrochloric acid. The acid solution was prepared from the neutral alcoholic solution by passing hydrochloric acid gas into it and was found to be about nine-tenths of the strength in didymium of the neutral solution.



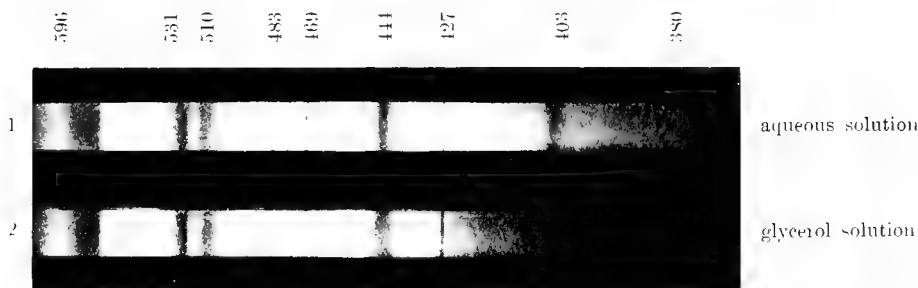
The general absorption at the more refrangible end is extended a little by the alcohol, and still more by the addition of acid.

The bands are generally rendered more diffuse by alcohol and a little shifted towards the red end of the spectrum, the shift increasing as the refrangibility decreases.

The acid seems to diffuse away the bands in the blue, the strong pair at about $\lambda 520$ are just visible in the spectrum of the acid solution considerably shifted towards the red. And the strong group in the yellow is still more shifted, and so spread out that several of the component bands are separated.

PLATE 18.

Absorptions by equivalent solutions of didymium nitrate in water and in glycerol.



No definite shift of the bands by the glycerol appears in the photograph, but there is an extension of the general absorption at the more refrangible end of the spectrum, and the bands are rendered more diffuse by the glycerol.

PLATE 19.

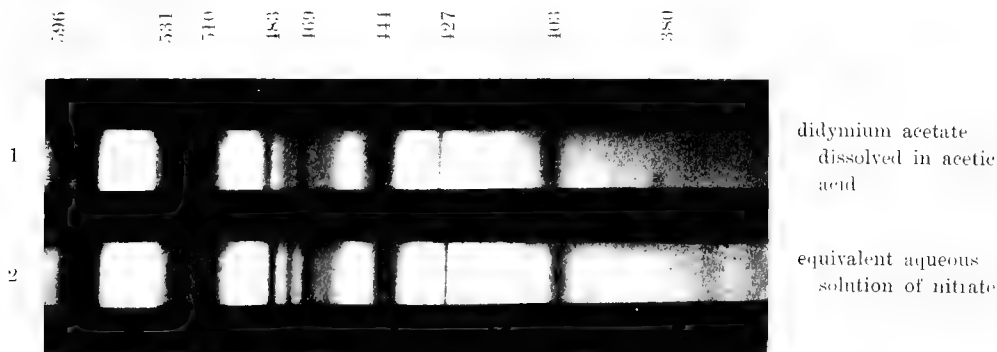
Absorptions by glass of borax coloured with didymium oxide and by a solution in water of didymium nitrate containing a quantity of didymium equal to that in the glass.



These photographs are disfigured with horizontal lines due to dust on the slit of the spectroscope. It will be seen that the bands are for the most part shifted by the borax but very unequally so; also that the bands are rendered more diffuse by the borax and some almost diffused away.

PLATE 20.

Absorptions by equivalent solutions of didymium acetate in acetic acid and of didymium nitrate in water.

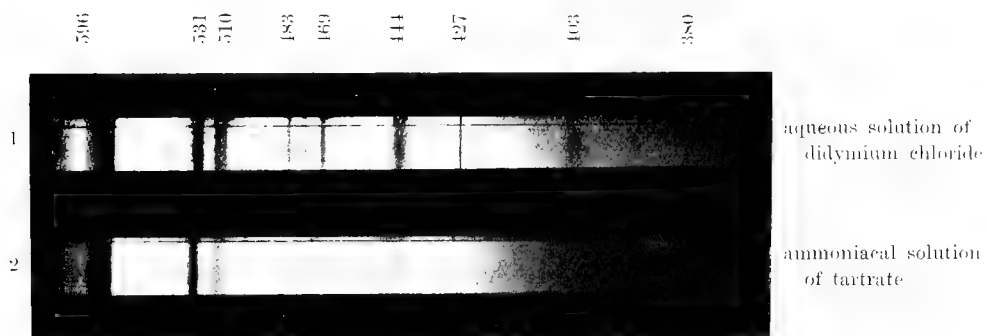


The bands are generally shifted towards the red by the acetic acid, and in the photograph the shift diminishes as the band is less refrangible; but the dispersion of the spectroscope also diminishes as the light is less refrangible; so the apparent diminution of the shift is not altogether real.

The acetic acid also increases the diffuseness of the bands, as is very manifest in the case of the band at about $\lambda 476$, and may be traced in others.

PLATE 21.

Absorptions by solutions of didymium chloride in water, and of didymium tartrate in water charged with ammonia.



The tartrate has all its bands more diffuse than the chloride, some of them almost diffused away, and they are shifted towards the red.

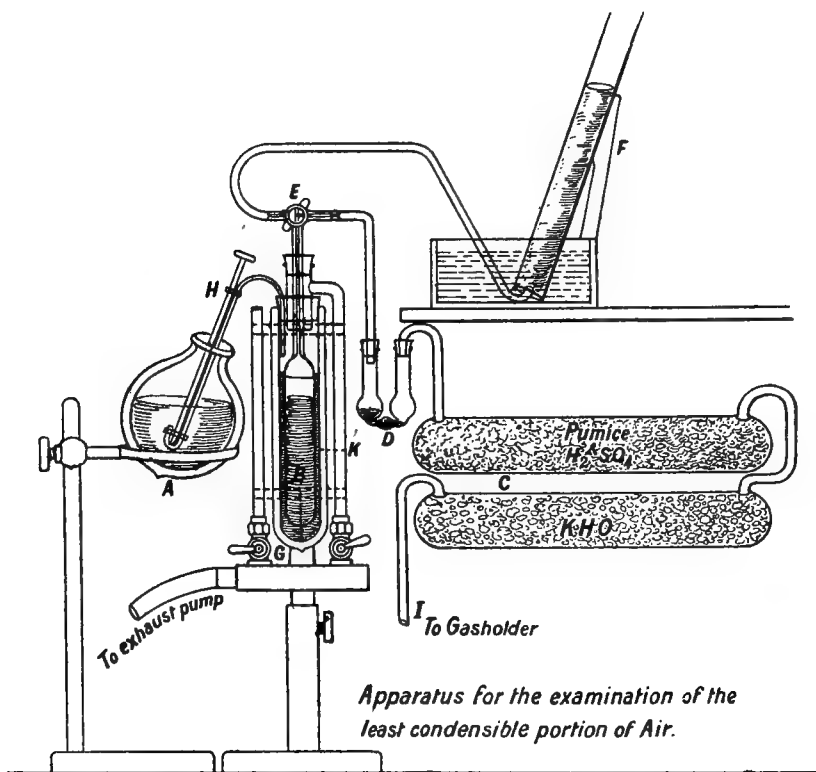
THE LIQUEFACTION OF AIR AND THE DETECTION OF IMPURITIES

[*Proceedings of the Chemical Society*, Vol. XIII. (1897), pp. 186 sqq.]

IN a paper on "The relative behaviour of chemically prepared, and of atmospheric nitrogen," read before the Society in the year 1894, it was stated that all samples of nitrogen and oxygen properly purified, are, when liquefied, clear transparent liquids, so that the solid matter which always separates when air or nitrogen or oxygen is liquefied on the large scale consists of impurities. Ordinary air, containing 4 parts of carbonic acid per 10,000 parts, gave a turbid liquid from the solidification of the carbonic acid; and oxygen containing traces of chlorine behaved in a similar manner. With the object of ascertaining the proportion of any gas that is not condensable at about -210°C . under atmospheric pressure, or is not soluble in liquid air under the same conditions, the following apparatus has been devised. A cylindrical bulb of a capacity of 101 c.c., marked *B* in the figure, had a capillary tube sealed into it terminating in a three-way stopcock, as shewn at *E*. The parts marked *C* and *D* consist of soda-lime and sulphuric acid tubes for removing carbonic acid and water. The stand marked *G* holds the large vacuum test tube into which *B*, which holds the liquid air maintained under continuous exhaustion, is inserted. As this low temperature had to be kept steady for from one to two hours, while at the same time the bulb *B* had to be completely covered with liquid air, it was necessary to arrange some means of keeping up the liquid air supply without disturbing the apparatus. The plan adopted is shewn at *H*, which is a valve arrangement which can be so regulated as to suck liquid air from the large vacuum vessel *A* and discharge it continuously along a pipe into the vacuum test tube *G*, the latter being kept under good exhaustion. In working the apparatus, the tube *I* is connected to a gasometer containing 10 cubic feet of air, so that the volume of air condensed in each experiment may be observed. This was generally from $2\frac{1}{2}$ to 3 cubic feet. If there is a very small proportion of some substance not liquefiable or soluble in liquid air, then we should expect

the vessel *B* would not fill up completely into the capillary tube. This is, however, exactly what does take place. After 40 minutes' cooling, the vessel *B* and the cool part of the tube were filled with liquid. In this experiment some 80 litres of air were condensed, and any accumulated uncondensed matter must have been concentrated in the upper part of the capillary tube which had a volume of 0.5 c.c. Under the conditions, therefore, the material looked for must be less than 1 part by volume in 180,000 of air.

To test the working with an uncondensable gas added to air, a volume of 10 cubic feet was taken in the gasholder and to that 500 c.c. of hydrogen were added. This is in the proportion of less than 1 in 500. Even after two hours' cooling, the tube *B* could only be filled four-fifths. In order to prove that the gas accumulated in the upper part of *B* was hydrogen, the three-way



stopcock at *E* was turned, and the temperature allowed to rise so that the gas was expelled by the evaporation of the liquid air and collected over mercury as shewn at *F*. The gas thus collected was easily combustible and consisted chiefly of hydrogen. The amount of hydrogen was then reduced to 1 part in 1000 of air, and it was found that after one and a quarter hours'

cooling the bulb *B* had filled to within a half c.c. of the capillary tube. A new sample of air containing 1 part of hydrogen in 10,000 of air filled the bulb *B* completely as if it were ordinary air.

It appears from these experiments that 1 part of hydrogen in 1000 of air is just detectable by this plan of working. As the 80 litres of air condensed contained some 80 c.c. of hydrogen, it appears that 100 c.c. of liquid air at from -200° to -210° C. had dissolved nearly all this gas; in fact, that 20 c.c. of hydrogen at the low temperature are dissolved in 100 c.c. of liquid air. In the paper on "The liquefaction of air and research at low temperatures" (*Proc. Chem. Soc.*, 1895, xi, 230), it was shewn that if hydrogen containing a small percentage of oxygen were employed for the purpose of getting a liquid hydrogen jet, the liquid collected from it was oxygen, containing, however, so much hydrogen dissolved in it that the gas coming off for a time was explosive.

In order to press this inquiry a little further, some natural gas known to contain a different constituent like helium suggested itself as being worthy of trial. Lord Rayleigh's results of the examination of the gas from the King's Well at Bath shewed that it contained 1.2 part of helium per 1000 volumes, so that it seemed admirably adapted for such experiments. The author has to express his thanks to the Corporation of Bath for giving permission to collect samples of the gas.

The sample of gas from the Bath Spring was treated exactly in the same way as the hydrogen mixtures described above. During the liquefaction there was a marked difference in the appearance of the liquefied gas, for while the hydrogen and air mixtures gave a clear, transparent liquid, the product from the Bath gas was turbid, and the precipitate by transmitted light looked yellow-brown. This solid turns out to be of organic origin, probably of the petroleum order of compounds. It has a very marked aromatic smell resembling such bodies. The trace of material left, gave, after treatment with concentrated nitric acid, the smell of nitrobenzene; and as its detection cannot be explained by the presence of any material of the kind in the vessels used in collecting, it must be assumed to be a normal constituent of the Bath gas. A further quantity of the Bath gas must be collected in order to confirm the presence of such bodies and to definitely make out their nature. Another peculiarity of the liquid is that, on examining it with the spectroscope, even through a thickness of 2 inches, no trace of the characteristic oxygen absorption spectrum could be detected. In all attempts to make nitrogen for liquefaction on the large scale, oxygen could always be detected in the liquid with the greatest ease by means of its absorption spectrum. After the cooling had continued for 1 hour the gas ceased to flow into the condensing vessel, and some 20 c.c. at the upper part of the glass cylinder *B* was filled with a gas that had not undergone liquefaction or solution. About

70 litres of the Bath gas were condensed, certainly the largest quantity of this gas ever subjected to chemical examination. This was boiled off just as the hydrogen was treated in the experiments described above, and as, by accident, too much nitrogen had volatilized along with the gas, oxygen was added and the mixture sparked over alkali to get rid of the excess of nitrogen. During the sparking, the helium lines were well marked (along with others the origin of which must be settled later), and a vacuum tube filled with the product of the sparking gave a splendid spectrum of the gas. The sample of gas directly collected from the liquid nitrogen contained about 50 per cent. of helium. It is therefore possible to separate helium from a gas when it is only present to the extent of one-thousandth part by liquefaction in the manner described.

APPLICATION OF LIQUID HYDROGEN TO THE PRODUCTION OF HIGH VACUA, TOGETHER WITH THEIR SPECTROSCOPIC EXAMINATION

[*Proceedings of the Royal Society*, Vol. LXIV. (1898), pp. 231 sqq.]

As an illustration of the extraordinary power of the new cooling agent—liquid hydrogen, the extreme rapidity with which high vacua can be produced by its use is, perhaps, one of the most striking. The absolute boiling points of hydrogen, oxygen, and chlorine are respectively 35°, 90° and 240°; in other words oxygen boils at a temperature two and a half times higher than liquid hydrogen, and liquid chlorine similarly at two and a half times that of liquid oxygen. From this we infer that liquid hydrogen as a cooling agent ought to be relative to liquid air as effective as the latter is compared to that of liquid chlorine. Now chlorine at the temperature of boiling oxygen is a hard solid, some 80° below its melting point, and in this condition has an excessively feeble vapour pressure. When liquid hydrogen freezes air out of a sealed tube by immersing the end in the liquid, it is to be inferred that no measurable pressure of air ought to be left in the vessel. If we apply Van der Waal's law of corresponding temperatures to the case of hydrogen, the above inference is made unimpeachable. An approach to some knowledge of what the tension of air must be about the boiling point of hydrogen can be attained by extrapolating the vapour pressure curves of oxygen and nitrogen. Taking the following range of boiling point temperatures for nitrogen and oxygen, viz., from the critical point to the boiling point under diminished pressure, two Willard Gibbs formulæ were calculated, with the following results:—

Nitrogen	Temp. abs.	127°	78·6°	59°
	Pressure in mm.	25,900	740	26
Nitrogen. $\log_{10} p = 11·5561 - \frac{400·02}{T} - 1·8980 \log_{10} T$(1).				
Oxygen	Temp. abs.	154°	90·3°	61·3°
	Pressure in mm.	37,592	740	7·5
Oxygen. $\log_{10} p = 9·4699 - \frac{422·22}{T} - 0·9843 \log_{10} T$(2).				

Another Gibbs formula was calculated, taking Estreicher's values for the vapour pressure of liquid oxygen below its boiling point, viz. :—

{Temp. abs.	91·44°	78·1°	62·8°
{Pressure in mm. ...	743·8	141·8	7·5

$$\text{Oxygen. } \log_{10} p = 16·0670 - \frac{524·72}{T} - 3·8024 \log_{10} T \dots\dots(3).$$

We deduce from these formulæ the following vapour pressures at the temperature of boiling hydrogen :—

(1) Nitrogen.....	0·0015	Pressure in mm., 35° abs.
(2) Oxygen	0·000076	do.
(3) „	0·000016	do.

The results of calculation, taking the formulæ for the widest range of pressures, viz. (1) and (2), may probably be the surest, but in any case those values must be taken as a *maximum*, seeing they refer to the liquid state, while both oxygen and nitrogen, at the temperature of 35° absolute, are hard solids, and must therefore have dropped to lower tensions than that of the extrapolated liquid vapour pressure curves. It is curious to note that at this low temperature the theoretical ratio of the tensions of nitrogen and oxygen is as 20 to 1. Direct measurements of the vapour pressure of nitrogen at the melting point, or 60° absolute, gave the value of 26 mm., and a ratio of the tensions of nitrogen to oxygen of 6 to 1, whereas from the curves the value ought to be 6·7 to 1. Olszewski gives the tension of nitrogen at -214° as 60 mm., and as at this temperature the oxygen tension is 3·8 mm., the ratio of the saturated pressures of the two gases at the melting point of nitrogen would be as 16 to 1, which is far too high. Probably the oxygen value will be nearest the truth, seeing it has the lowest melting point. The tension is about a ten millionth of an atmosphere. In the case of nitrogen, the maximum theoretical pressure would be one five-hundred-thousandth of an atmosphere. It is safe to infer that the vacuum left after liquefying the air out of a vessel by means of liquid hydrogen cannot exceed the millionth part of the atmospheric pressure, exclusive of the pressure resulting from any incondensable material other than nitrogen and oxygen. This is just about the pressure of the vapour of mercury at the ordinary temperature in the Torricellian vacuum, so that as good an exhaustion ought to result as can be got by boiling out a space with mercury. There is another way in which the question may be put. Assuming the molecular latent heats are approximately proportioned to the absolute boiling points, then we can, from a comparison with the oxygen value, deduce that of hydrogen, and thereby get the constants in a two-term formula for the vapour pressures. For pressures below an atmosphere, the following approximate formulæ were deduced :—

$$\text{Oxygen..... } \log p = 7·2058 - \frac{392·6}{T} \text{ mm. } \dots\dots\dots(4).$$

$$\text{Hydrogen... } \log p = 7.2428 - \frac{152.7}{T} \text{ mm. (5).}$$

From these expressions it follows that at its boiling point, or 35° absolute, hydrogen has 7/852000 times the pressure of oxygen, or the latter pressure is about the eight millionth of an atmosphere. A similar formula, calculated from the critical and boiling point data, gives substantially the same order of quantities. Formula (4) for oxygen tensions must be fairly accurate, seeing it gives a theoretical latent heat of about 56 units per gram of liquid evaporating at the boiling point, whereas direct determinations result in 55 units. To test this inference, the following plan of experimenting was adopted:— Ordinary shaped vacuum tubes, like *A*, *B*, used for the spectroscopic exami-

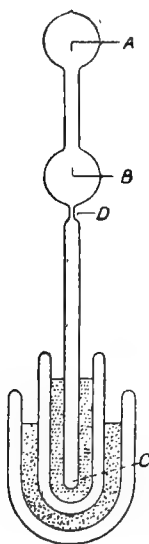


FIG. 1.

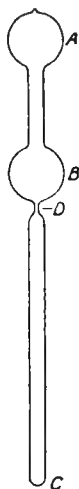


FIG. 2.

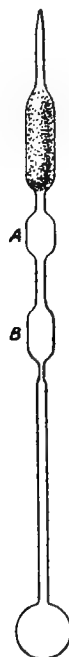


FIG. 3.

nation of gases, with and without electrodes (figs. 1 and 2), having a capacity ranging from 15 to 25 c.c., had pieces of quill tubing about a foot long sealed on. The tubes were contracted at *D* to about 1 mm., so that they could be sealed off with rapidity. The end *C* sometimes terminated in a small bulb (fig. 3), in order to give increased cooling surface, and, when necessary, to allow many times the volume of air in *A*, *B* to enter and be condensed with the object of accumulating any incondensable residuum.

The tubes were filled with air, oxygen, and nitrogen at the atmospheric pressure. The liquid hydrogen collected in the vacuum vessel, immersed in

another similar vessel full of liquid air, being ready, the end *C* was dipped in the liquid for a little over a minute, and the tube *AB* sealed off at *D*, so that on removal from the hydrogen bath the solid air might melt and distil off without generating any pressure. On attempting to pass the spark through vacuum tubes prepared in this manner, their excellent exhaustion was revealed by great resistance to the passage of the discharge, and the high phosphorescence of the glass. Two tubes, kindly prepared by Sir William Crookes with platinum electrodes that he had previously sparked to remove gases and impurities on the glass before filling with dry air, gave, when treated in the manner described, such high vacua that the tubes had to be heated in order to get any spark to pass. Thus it is proved that the tension of solid nitrogen and oxygen at the temperature of boiling hydrogen is below the millionth of an atmosphere, seeing there is less difficulty in getting a discharge to pass in tubes exhausted to this extent. In order to get some definite idea of the limit of the exhaustion produced, two tubes, such as have been described as suitable for the liquid hydrogen experiments, might be joined together and filled with oxygen or nitrogen at atmospheric pressure, and simultaneously exhausted with the mercurial pump to a small fraction of an atmosphere, and then sealed off from the pump and each other. One of these two identical tubes could then be subjected to the hydrogen cooling, following the directions already given, and the two vacuum tubes now compared. If there was a marked difference in resistance to the passage of the discharge in the frozen tube, then something must have condensed, and by a few tentative trials a limit might be reached when the initial exhaustion was unaffected by the hydrogen cooling. Such experiments have not yet been made. The presence of any vapour of mercury would require to be carefully eliminated, otherwise the method would not be satisfactory. Tubes that are prepared without taking special precautions to exclude organic matter and water from the glass, deteriorate, especially with electrodeless tubes, after the discharge has taken place for some time.

The rapidity with which the vacua are attained is such as theory would suggest; assuming a hole of a square millimetre in section through which the air rushes into the condenser, and that a velocity of current between 600 and 700 feet a second is attained, then a vessel of 20 c.c. capacity could be reduced in pressure in 1 second to $1/10$ of the initial pressure, and if the same rate is continued at the end of 60 seconds to $(\frac{1}{10})^{60}$. Sir George Stokes has been good enough to consider the problem and writes as follows:—

“Let *V* be the volume of the vessel, *A* the area of an aperture by which the air is conceived as rushing out with the velocity *v*, *ρ* the density of the air in the vessel at the time *t*, *D* the initial density, that is, the atmospheric density.

“Then, according to our hypothesis, *A**v*.*dt* is the volume of air, and, therefore, *A**v**ρ*.*dt*, the mass of air, which rushes out in the time *dt*. But

this equals the loss of mass of air in the vessel during the time dt , and, therefore,

$$Av\rho \cdot dt = -Vd\rho,$$

a differential equation of which the integral is

$$\rho = De^{-Avt/V}.$$

"Suppose now V to be 20 c.c., or 20,000 c.mm., A to be the area of a circle of 1 or 2 mm. diameter, say 2 sq. mm., v to be 333 m., or 333,000 mm., t (in seconds) to be 60; then

$$\log_e \frac{D}{\rho} = \frac{2 \times 333,000 \times 60}{20,000} = 1998,$$

$$\frac{D}{\rho} = 5254 \times 10^{44}.$$

"This would give a density of almost inconceivable smallness. Doubtless the supposition made above as to the rate of discharge is very wide of the mark, being much too great. If the velocity of rushing is about half the velocity of sound, the ratio of densities would become 72×10^{217} . If so it is satisfactory to find that the mathematical following out of the hypothesis leads to a density of the residual air in the vessel which is enormously below what suffices to account for the observed result." A practical mode of rapidly attaining a high vacuum in any vessel is to displace the air with carbonic or sulphurous acid, either at the atmospheric or under diminished pressure, and then to freeze out the remaining gas by the use of liquid air, just as in the experiments with liquid hydrogen.

The first vacuum tube was an electrodeless one, the air had not been dried, nor the glass specially cleaned. On spectroscopic examination it shewed hydrogen lines bright along with the second or compound line spectrum of the same gas, and a series of bright bands defined on the less refrangible side, diffuse on the more refrangible, which occur in the yellow, green, blue, and indigo. These bands were found to be identical with the carbonic oxide spectrum. With a Leyden jar in the secondary circuit the line spectrum of hydrogen disappeared, leaving the second spectrum fainter; but the carbonic oxide bands remained bright, and there was no appearance of the hydrocarbon spectrum. The second tube had aluminium electrodes, and, like the last, had no special treatment in filling in the air. This tube shewed also the line spectrum and the second spectrum of hydrogen; the latter being bright along with the carbonic oxide spectrum; but on sparking the latter disappeared. No appearance of the hydrocarbon spectrum could be detected, but there was a suspicion of bands in the indigo like the negative pole spectrum of nitrogen. The addition of a Leyden jar brought out nothing new, only intensifying the line spectrum of hydrogen, while leaving the second spectrum bright. In neither of the above tubes could any lines of

nitrogen or oxygen be recognised. The third tube was filled with air drawn over cotton wool, red-hot copper oxide, and phosphoric pentoxide, no rubber joints being employed. The spectrum shewed the carbonic oxide bands and the hydrogen line spectrum as before. Only the second hydrogen spectrum was feeble. There was a yellow line wave-length 5849, identical with one occurring in the natural gas from the King's Well at Bath. In a paper on "The Liquefaction of Air and the Detection of Impurities*," the separation of helium from this gas is described by liquefaction and fractionation, and it was observed that during the sparking the helium lines were well marked along with "*others, the origin of which must be settled later.*" It was further observed, "*With a modified form of apparatus it will be possible to collect any residuary gas from the use not of 3 cubic feet of air or Bath gas, but from hundreds of cubic feet of such products.*" The helium and other associated material was shewn to be more volatile than nitrogen. Pursuing this course of investigation in the summer of this year, the volatile portion of air was examined, when the presence of material giving the same lines as Bath helium was recognised. While this investigation was in progress, Professor Ramsay and Dr Travers observed the same spectrum in the more volatile portion of argon which they have associated with a new element called neon. The use of liquid hydrogen, as described, proves that the most characteristic line of neon in the yellow, about wave-length 5849, can be detected in 25 c.c. of ordinary air, and the presence of helium in the atmosphere is confirmed†.

A fourth tube, filled like the preceding one, had a phosphoric pentoxide tube left on. This shewed again the carbonic oxide bands, but no hydrogen lines could be detected; while the oxide of copper ought to have removed all free hydrogen and transformed all the organic matter into carbonic acid and water. Yet it appears that the spectrum of the carbon compounds is difficult to remove from electrodeless tubes, probably owing to carbonic acid coming from the glass. There were some broad diffuse bands that may arise from the drying agent. The absence of hydrogen in this tube suggests that its presence in the third tube was due to vapour of water coming slowly from the glass. I am greatly indebted to Professor Liveing for making a careful examination of the spectra of these tubes.

Sir William Crookes was good enough to prepare two tubes with platinum electrodes, which he sparked in vacua till all hydrogen disappeared, and then filled with dry air, but without the use of red-hot copper oxide or any agent for the absorption of carbonic acid or the destruction of organic matter.

* *Supra*, p. 476.

† In a paper along with Professor Liveing, "On the Spectra of the Electric Discharge in Liquid Oxygen, Air, and Nitrogen," *Phil. Mag.*, 1894, we noted that, during the distillation and concentration *in vacuo* of liquid oxygen and air under diminished pressure, two bright lines appeared in the spectrum at wave-lengths 557 and 555, and that one of these lines was very near the position of the auroral line. These lines are now attributed by the same chemists to a new element, krypton.

After the cooling with liquid hydrogen, he found on spectroscopic examination, in one no hydrogen, but two faint lines, one about wave-length 5852, and the other wave-length 5676. The second tube shewed the same yellow about 5852, the helium line along with 5939 and 6145, the hydrogen lines C and F, and some red lines. The observations of Crookes confirm the presence of neon, helium, and hydrogen. The absence in his tubes of the carbonic oxide spectrum is important, seeing all the electrodeless tubes gave this spectrum. In these tubes the vacuum was very high, and it was difficult to observe the gaseous spectrum. Still, the fact of finding hydrogen in one and not in the other, leaves the presence of free hydrogen in the atmosphere as a question for further inquiry. The tube that did not contain hydrogen was heated very hot in order to get a discharge, and then the spectrum shewed some bands like the negative glow of nitrogen. Occasionally, a jar discharge was got to pass, and when this took place the nitrogen lines could be seen. An electrodeless tube filled carefully with oxygen made from fused chlorate of potash, which was contained in an extension of the vacuum tube, gave nothing but the carbonic oxide bands. In future experiments it will be easy to concentrate all the most volatile material in air or other gases, and thereby to make a more thorough examination of the spectrum. In the meantime my object is to shew one of the scientific uses of liquid hydrogen.

I have to thank Mr Robert Lennox for efficient aid in the conduct of the difficult experiments. Mr Heath has also helped in the work.

ON THE SPECTRUM OF THE MORE VOLATILE GASES OF
ATMOSPHERIC AIR WHICH ARE NOT CONDENSED AT
THE TEMPERATURE OF LIQUID HYDROGEN.—PRELIMINARY
NOTICE

[*Proceedings of the Royal Society*, Vol. LXVII. (1900), pp. 467 sqq.]

IN August last some tubes were filled at low pressure by an improved process with the more volatile gases of the atmosphere*. The air was liquefied directly from that above the roof of the Royal Institution by contact at atmospheric pressure with the walls of a vessel cooled below -200°C . When about 200 c.c. of liquid had condensed, communication with the outer air was closed by a stop-cock. Subsequently, communication was opened, through another stop-cock, with a second vessel cooled by immersion in liquid hydrogen, and a part of the liquid from the first vessel, maintained at -210° , was allowed to distil into the second still colder vessel. When about 10 c.c. had condensed in the solid form in the second vessel, communication with the first vessel was cut off, and the manometer shewed a pressure of gas of about 10 to 15 mm. of mercury.

This mixture of gases was passed into tubes previously exhausted by a mercury pump, but before reaching the tubes it had to pass through a U-tube immersed in liquid hydrogen so as to condense less volatile gases, such as argon, nitrogen, oxygen, or carbonic oxide, which might be carried along by those more volatile. Previous trials with tubes filled in the same way, except that the U-tube in liquid hydrogen was omitted, shewed that these tubes contained traces of nitrogen, argon, and compounds of carbon. The tubes filled with gas which had passed through the U-tube shewed on sparking no spectrum of any of these last-mentioned gases, but shewed the spectra of hydrogen, helium, and neon brilliantly, as well as a great many less brilliant rays of unknown origin. In addition, they shewed at first the brightest rays of mercury, derived, no doubt, from the mercury pump by which they had

* In this paper we describe researches in continuation of those previously communicated to the Society by one of us, in the preceding paper.

been exhausted before the admission of the gases from the liquefied air. After some sparking the mercury rays disappeared, probably in consequence of absorption of the mercury by the electrodes, which were of aluminium.

In one experiment the mixture of gases in the second vessel, into which a fraction of the liquefied air was distilled as above described, was pumped out without being passed through the U-tube in liquid hydrogen and examined. This mixture was found to contain 43 per cent. of hydrogen, 6 per cent. of oxygen, and 51 per cent. of other gases—nitrogen, argon, neon, helium, etc.—and it was explosive when mixed with more oxygen. This shews conclusively that hydrogen in sensible proportion exists in the earth's atmosphere, and if the earth cannot retain hydrogen or originate it, then there must be a continued accession of hydrogen to the atmosphere (from interplanetary space), and we can hardly resist the conclusion that a similar transfer of other gases also must take place. The tubes containing the residue of atmospheric gases uncondensed at the temperature of liquid hydrogen we have examined spectroscopically.

On passing electric discharges through them, without any condenser in the circuit, they glow with a bright orange light, not only in the capillary part, but also at the poles, and at the negative pole in particular. The spectroscope shews that this light consists in the visible part of the spectrum chiefly of a succession of strong rays in the red, orange, and yellow, attributed to hydrogen, helium, and neon. Besides these, a vast number of rays, generally less brilliant, are distributed through the whole length of the visible spectrum. They are obscured in the spectrum of the capillary part of the tube by the greater strength of the second spectrum of hydrogen, but are easily seen in the spectrum of the negative pole, which does not include the second spectrum of hydrogen, or only faint traces of it. Putting a Leyden jar in the circuit, while it more or less completely obliterates the second spectrum of hydrogen, also has a similar effect on the greater part of these other rays of, as yet, unknown origin. The violet and ultra-violet part of the spectrum seems to rival in strength that of the red and yellow rays, if we may judge of it by the intensity of its impressions on photographic plates. We were surprised to find how vivid these impressions are up to a wave-length 314, notwithstanding the opacity of glass for rays in that part of the spectrum. The photographs were taken with a quartz calcite train, but the rays had to pass through the glass of the tube containing the gases.

We have made approximate measurements of the wave-lengths of all the rays which are sufficiently strong to be seen easily or photographed with an exposure of thirty minutes, and give a list of them below. These wave-lengths are computed to Rowland's scale, and were deduced from the deviations produced by two prisms of white flint glass for the visible, and of calcite for the invisible, rays. The wave-lengths assigned to the helium lines are

those given by Runge and Paschen, and some of these lines were used as lines of reference. In general, the iron spark spectrum was the standard of reference.

The tubes when first examined shewed the lines of the first spectrum of hydrogen vividly, and the earlier photographs of the spectrum of the negative pole contained not only the violet lines of hydrogen, but also the ultra-violet series as far up as $\lambda 377$. In order to get impressions of the fainter rays, exposures of half an hour or more were required, and a succession of photographs had to be taken so as to get different sections of the spectrum into the middle of the field, where measurement of the deviations would not be impeded by the double refraction of the calc spar. As the light of the negative pole only was required, the electric discharge was made continuously in one direction only, with the result that the hydrogen lines grew fainter in each successive photograph, and soon disappeared altogether. Along with the ultra-violet rays, the less refrangible rays of hydrogen also disappeared, so that no trace of the C or F line could be seen, nor yet of the second spectrum, so long as the current passed in the same direction as before. Reversal of the current soon made the F line shew again, so that it seems that the whole of the hydrogen was driven by the current to the positive pole. The conditions under which this ultra-violet series shews itself are a matter of interest. It appears here in the midst of a brilliant spectrum due to gases other than hydrogen, and yet it is very difficult to obtain a photograph of it when no gas but hydrogen is known to be present, or, at least, to become luminous in the electric discharge.

We have had an opportunity of comparing the spectrum of the volatile residue of air with that of the more volatile part of gas from the Bath spring. The tube did not admit of the separate examination of the light from the negative pole, but was examined end-on, so that the radiation probably included rays emitted from the neighbourhood of the negative pole. The whole of the hydrogen had been removed from the Bath gas, but not all the argon. In the spectrum of this gas the rays of helium are dominant, decidedly stronger than those of neon, although the latter are very bright. In the spectrum of the residue of atmospheric air, the proportion of helium to neon seems reversed, for in this the yellow neon line is as much more brilliant than the yellow helium line as the latter is the more brilliant in the spectrum of Bath gas. All the prominent lines in the spectrum of the volatile residue of Bath gas were also in that of the residue of atmospheric air, except the argon lines. There were, on the other hand, many lines in the latter not traceable in the former, some of them rather conspicuous, such as the ray at about $\lambda 4664$. It is, of course, probable that such rays are the outcome of some material not contained in the Bath gas. A very conspicuous pair of lines appears in photographs of the spectrum of the air residue, at about $\lambda 3587$, which is not traceable in the spectrum of Bath gas. The helium line, $\lambda 3587.4$,

is seen in the latter spectrum, but is quite obscured in the former spectrum by the great intensity of the new pair. This helium ray is really a close double, with the less refrangible component much the weaker of the two, but the new pair are wider apart, and of nearly equal intensities; this character also distinguishes them from the strong argon line at $\lambda 3588.6$. They are, however, very much more intense at the negative pole than in the capillary, and it will require a good deal more study to determine whether these rays, and many others which we have not tabulated, are due to the peculiarity of the stimulus at the negative pole, or to the presence of a previously unrecognised material.

As our mixture of gases probably includes some of all such gases as pervade interplanetary and interstellar space, we early looked in their spectra for the prominent nebular, coronal, and auroral rays. Searching the spectrum about $\lambda 5007$ no indication of any ray of about that wave-length was visible in the spectrum of any one of the three tubes which had been filled as above described. Turning to the other green nebular line at about $\lambda 4959$, we found a weak rather diffuse line to which our first measure assigned a wave-length 4958. The correctness of this wave-length was subsequently verified by measuring with a micrometer eye-piece the distances of the line from the helium lines $\lambda 4922.1$ and $\lambda 5015.7$ which were in the field of view at the same time. The position of the line was almost identical with that of the iron spark line $\lambda 4957.8$, and the conclusion arrived at was that the wave-length was a little less than 4958, and that it could not be the nebular line. There remained the ultra-violet line $\lambda 3727$. Our photographs shewed a rather strong line very close to the iron spark line $\lambda 3727.8$, but slightly more refrangible. As the line is a tolerably strong one, it could be photographed with a grating spectrograph along with the iron lines. This was done, and the wave-length deduced from measuring the photograph was 3727.4. This is too large by an amount which considerably exceeds the probable errors of observation, and we are forced to conclude that the nebular material is either absent from our tubes, or does not shew itself under the treatment to which it has been subjected.

Although the residual gases of the atmosphere uncondensed at the temperature of liquid hydrogen do not shew the nebular lines, we found that another tube gave a ray very close indeed to the principal green nebular ray. This tube had been filled with gas prepared in the same way as the others, with the exception that, in passing from the vessel into which the first fraction of liquid air was distilled, it was not passed through a U-tube immersed in liquid hydrogen on its way to the exhausted tube. In consequence it contained traces of nitrogen and argon, and when sparked shewed the spectra of these elements as well as those of hydrogen, helium, etc. The nitrogen spectrum disappeared after some sparking, but the tube still shews rays of argon as well as those of the gases in the other tubes. On examining

the spectrum of the negative pole in the neighbourhood of the principal nebular green ray, a weak ray was seen in addition to those given by the other tubes. It was found by comparison with the nitrogen rays $\lambda 5002\cdot7$ and $\lambda 5005\cdot7$ to be a little less refrangible than the latter of these rays, and by measuring its distance from the nitrogen rays and from the two helium rays $\lambda 4922\cdot1$ and $\lambda 5015\cdot7$ with a micrometer eye-piece, the wave-length $\lambda 5007\cdot7$ for the new ray was deduced. This looks as if we might find the substance which is luminous in nebulae to be really present in the earth's atmosphere, and we hope shortly to be able to verify the observation of it.

Turning to the coronal rays, our tubes emit a weak ray at about $\lambda 5304$. This is not far from the wave-length $\lambda 5303\cdot7$ assigned by Sir N. Lockyer to the green coronal ray. It is, however, greater than that assigned by Campbell, namely, $5303\cdot26^*$. Other lines observed by us near the places of coronal lines are at wave-lengths about 4687, 4570, 4358, 4323, 4232, 4220, 3985, 3800. These are all weak lines except that at $\lambda 4232$, which is of tolerable strength, and that at $\lambda 4220$, which is rather a strong line. The wave-lengths 4323, 4232, 4220, and 3800 come very close to those assigned to coronal rays, but the others hardly come within the limits of probable error. The ray 4220 seems too strong in proportion to the others, but the strength of that at 4232 seems to accord with the strength of the corresponding ray in the corona. It will be seen that the rays we enumerate above correspond approximately to the stronger rays in Sir N. Lockyer's list†. Further measures of the wave-lengths of the faint lines are needed before we can say definitely whether or no we have in our tubes a substance producing the coronal rays, or some of them.

As to the auroral rays, we have not seen any ray in the spectrum of our tubes near $\lambda 5571\cdot5$, the green auroral ray. We have observed two weak rays at $\lambda 4206$ and $\lambda 4198$ which may possibly, one or both, represent the auroral ray $\lambda 420$. The very strong ray of argon, $\lambda 4200\cdot8$, would make it probable that argon was the origin of this auroral ray, if the other, equally strong, argon rays in the same region of the spectrum were not absent from the aurora. Nor have we found in the spectrum of our tubes any line with the wave-length 3915, which is that of another strong auroral line. On the other hand it seems probable that the strong auroral line $\lambda 358$ may be due to the material which gives us the very remarkable pair of lines at about the place of N of the solar spectrum, $\lambda 3587$, which are very strong in the spectrum of the negative pole, but only faint in that of the capillary part of our tubes. It may well be that the auroral discharge is analogous to that about the negative pole. We have also a fairly strong ray at $\lambda 3700$, which may be compared to the remaining strong ray observed in the aurora $\lambda 3700$. This, however, is a ray which is emitted from the capillary part of our tubes as

* *Astroph. J.*, Vol. x, p. 190.

† *Roy. Soc. Proc.*, Vol. lxvi, p. 191.

well as from the negative pole, and is, moreover, emitted by Bath gas, and may very likely be a neon ray.

We hope to pursue the investigation of this interesting spectrum, and if possible to sort out the rays which may be ascribed to substances such as neon and those which are due to one or more other substances. The gas from Bath, even if primarily derived from the atmosphere—which is by no means sure—seems to have undergone some sifting which has affected the relative proportions of helium and neon, and a more thorough comparison of its spectrum with that of the residual atmospheric gases may probably lead to some disentanglement of the rays which originate from different materials. The arrangement of the rays in series, if that could be done, would be a step in the same direction.

We are indebted to Mr Robert Lennox, F.C.S., for the great help he gave us in the complicated manipulation with liquid hydrogen required to fill the spectral tubes, and to Mr J. W. Heath, F.C.S., for kind assistance.

List of Approximate Wave-lengths of the Rays, Visible and Ultra-violet, observed about the Negative Pole.

The rays of hydrogen and helium, and those attributed to neon by other observers, are indicated by the chemical symbols of those substances:—

A “b” prefixed to the number expressing the wave-length indicates that the ray is emitted by gas from the Bath spring as well as by that obtained from the atmosphere.

A “c” similarly prefixed indicates that the ray has been observed to be emitted from the capillary part of the tube as well as from about the negative pole.

A “w” indicates a weak line; “s” a strong one; “d” a diffuse one; “vw” a very weak one; and “vs” a very strong one.

bc He	7281·8	bc Ne	6508	bc Ne	6163
	7247	vwbc	6446	bc Ne	6144
	7174	bc Ne	6404	vwbc	6128
bc He	7065·5	bc Ne	6382	b Ne	6097
vw	7058	bc Ne	6334	b Ne	6075
bc Ne	7034	bc Ne	6304	b Ne	6031
bc Ne	6931	bc Ne	6266	b	6001
bc Ne	6716	bc	6244	b	5991
bc He	6678·4	bc	6232	wb	5987
bc Ne	6601	bc Ne	6217	bc Ne	5976
sc H	6563	b	6183	wb	5964
bc	6535	vwbc	6176	sdb Ne	5945

w	5919	wb	4657	b	4131
w	5914	w	4647	wb	4128
wb	5905	wb	4640	b He	4121
bc	5882	w	4636	w	4112
bc He	5875·9	w	4628	sc H	4102
vsbc Ne	5852·7	w	4616	w	4099
sb	5820	w	4589	vw	4086
slb	5804	w	4583	w	4080
sbc	5763		4576	w	4063
bc	5747	w	4570		4047
bc	5718		4540	vw	4043
bc	5689		4538	vw	4037
wbc	5662	w	4526	vsbc He	4026·3
bc	5656	w	4523	b He?	4009
	5592	w	4518	w	3996
b	5561	w	4508	vw	3985
	5532	w	4500	vw	3980
vwb	5503	w	4488	sc H	3970
vw	5447	vs He	4471·6	s He	3964·9
wb	5432	vw	4460	vw	3933
vw	5417		4457	b? He?	3927
vwb	5409	vw	4438		3905
b Ne	5400	wb He	4437·7		3900
	5372		4431	vsbc He	3888·8
	5360		4429	wbc He?	3872
	5355		4424	bc He	3867·6
bc Ne	5341 a pair		4422	w	3866
bc Ne	5330		4413	w	3862
w	5304		4409	wc?	3860
w	5298		4398	w	3856
	5234		4392	w	3842
b	5222	b He	4388·1	w	3840
	5209		4380	c H	3836
b Ne	5204	w	4370	b	3830
b	5192	vw	4365	sbc He	3819·75
b Ne	5188	w	4363	wc He?	3806
	5152	w	4358	w	3800
b Ne	5145	vw	4347	c H	3798
	5122	s H	4340·7		3777
b Ne	5116	w	4334	w H	3770
b Ne	5080	vw	4322		3766
	5074	vw	4315		3754
b He	5047·8	vw	4306		3751
sbc	5038	w	4290	vw	3745
	5031		4276	w	3738
b He	5015·7	w	4270	? c	3735
wd	4958	w	4261	? c	3728
b He	4922·1	w	4258	w	3722
vw	4884		4251	w	3721·5
sc H	4861·5		4241	s	3713
vwb	4838		4234		3710
vw	4819		4232	bc He	3705·2
vwb	4811		4220	w	3703
wd	4791	w	4218		3701
wd	4754	w	4206	s c?	3694
b Ne	4715	vw	4198	c	3686
b Ne	4710	wc	4176	c	3683
b Ne	4704	wb He	4169·1	sc	3664
w	4687	w	4151		3655
w	4680	b He	4143·9		3651
	4664	w	4134	w	3650

sc He?	3644 a pair	bc	3464	w	3344
vw	3634 a pair	bc	3460	s	3335
bc He	3628	w	3456		3329
w	3613·8	bc	3454		3327
bc He?	3609	wc	3451	s	3324
sbc	3600	sbc He	3447·7	sb	3319
vs	3593	w	3429	w	3315
	3587·5 a pair	w	3424	w	3313
w	3575	sbc	3418	w	3311
	3571	vw	3417		3310
w	3569	w	3407	b He?	3297
w	3561	w	3404	vw	3254
w	3558	b	3393	wb	3250
vwb	3548	b	3388	s	3244
	3543	s	3378		3233
vsbc	3521	vw	3374	? pair	3230
bc	3515	w	3372		3225
wbc	3510	bc	3370	s	3218
w	3504		3367		3214
bc	3500	w	3363		3209
bc He?	3498	vw	3362		3199
	3482		3360	sb He	3187·8
	3481		3358	w	3165
sbc	3473	b He	3354·7	w	3142
bc	3467	s	3345		

ON THE MOST VOLATILE GASES OF THE ATMOSPHERE

[*Proceedings of the Cambridge Philosophical Society*,
Vol. XI. (1901), pp. 107, 108]

ATMOSPHERIC air, at ordinary pressure, was liquefied directly by contact with the walls of a vessel cooled below $-200^{\circ}\text{C}.$; when about 200 c.c. of liquid had condensed, communication with the atmosphere was closed, and a fraction of the liquid, still kept at $-210^{\circ}\text{C}.$, allowed to distil into a second, still colder, vessel immersed in liquid hydrogen. When about 10 c.c. had collected in the second vessel, in the solid state, communication between the two vessels was closed, and the gas above the solid in the second vessel was found to have a pressure of 10 to 15 mm. of mercury. Some of this gas was pumped out, and 43 per cent. of it was found to be hydrogen. Also tubes previously exhausted and sparked to remove hydrogen from the electrodes, and then filled with gases from the liquid air, at atmospheric pressure, gave the spectrum of hydrogen very strongly. Calculated as a percentage by volume of the atmosphere, hydrogen is present in very small quantity, nevertheless it forms a sensible percentage, and accords with the supposition that there is an interchange of gases by diffusion between our atmosphere and interplanetary space.

In other experiments the gas above the solid in the second vessel was allowed to pass through a U-tube cooled in liquid hydrogen into tubes previously exhausted; and the spectra given by electric discharges through them examined. These spectra are brilliant with the red, orange and yellow rays of helium and neon, but shew besides a vast number of other rays, belonging to substances hitherto unknown, which are most brilliant at the violet end, so that they can be photographed, notwithstanding the opacity of the glass tubes, up to a wave-length 3142. Their brilliance depends on the character of the discharge, and is greatest about the negative pole, and with no Leyden jar in circuit.

These spectra were searched for the characteristic nebular, coronal, and auroral rays. Tubes filled as above described shew no ray at about the wave-length 5007, the brighter green ray of nebulae, though they give a weak ray near, but not in the exact position of the other green nebular ray, λ 4959, and

a strong ray close to the strongest ultra-violet nebular ray $\lambda 3727$. A tube which had been filled with gas from the second vessel, without first passing through the U-tube cooled in liquid hydrogen, shewed a ray which seemed to be identical in position with the brighter green nebular ray; so that it is probable that the nebular stuff may yet be found in the earth's atmosphere.

The evidence of the existence in the earth's atmosphere of the gas, or gases, which produce the spectrum of the solar corona is stronger, for not only do the spectra of the most volatile atmospheric gases include a ray which fits, within the limits of probable error of observation, the place of the chief green coronal ray, but several other rays which correspond with strong rays which have been observed in the corona.

No ray, however, has been traced in these spectra, corresponding to the green auroral ray, which is perhaps due to the less volatile gas krypton. On the other hand one of the strongest rays, emitted mainly at the negative pole, at $\lambda 3587$, is at about the place of a strong auroral ray, and the authors suggest that the electric discharges to which the aurora is due may be of a nature similar to that which makes the glow about the negative pole in an exhausted tube.

The spectra suggest the presence of more than one unknown substance in the most volatile portion of the atmosphere, but further observations are needed to unravel their complexity.

ON THE SEPARATION OF THE LEAST VOLATILE GASES OF ATMOSPHERIC AIR, AND THEIR SPECTRA

[*Proceedings of the Royal Society*, Vol. LXVIII. (1901), pp. 389 sqq.]

OUR last communication to the Society* related to the more volatile of the atmospheric gases, that which we now beg leave to offer relates to the least volatile of those gases. The former were obtained from their solution in liquid air by fractional distillation at low pressure, and separation of the condensable part of the distillate by cooling it in liquid hydrogen. The latter were, in the first instance, obtained from the residue of liquid air, after the distillation of the first fraction, by allowing it to evaporate gradually at a temperature rising only very slowly. The diagram, fig. 1, will make the former process intelligible. *A* represents a vacuum-jacketed vessel, partly filled with liquid air, in which a second vessel, *B*, was immersed. From the bottom of *B* a tube, *a*, passed up through the rubber cork which closed *A*, and from the top of *B* a second tube, *b*, passed through the cork and on to the rest of the apparatus. Each of these tubes had a stop-cock, *m* and *n*, and the end of tube *a* was open to the air. A wider tube also passed through the cork of *A* and led to an air-pump, whereby the pressure above the liquid air in *A* was reduced, and the temperature of the liquid reduced by the consequent evaporation. To keep the inner vessel, *B*, covered with liquid, a fourth tube, *r*, passed through the cork, and its lower end, furnished with a valve, *p*, which could be opened and closed by the handle *q*, dipped into liquid air contained in the vessel *C*. As the pressure above the liquid in *A* was less than that of the atmosphere, on opening the valve *p* some of the liquid air was forced through *r* into *A* by the pressure of the atmosphere, and in this way the level of liquid in *A* maintained at the required height.

Since *B* was maintained at the temperature of liquid air boiling at reduced pressure the air it contained condensed on its sides, and when the stop-cock *n* was closed and *m* opened, more air passed in through the open

* *Supra*, p. 484.

end of *a*, and was in turn condensed. In this way *B* could be filled completely with liquid air, the whole of the most volatile gases being retained in solution in the liquid.

The tube, *b*, passing from the top of *B*, was connected with a three-way stop-cock *d*, by which it could be put in communication with the closed vessel, *D*, or with the tube *e*, by which also *D* and *e* could be connected at will either with each other only, or both at once with *b*. The tube *e* passed down nearly to the bottom of the vacuum-jacketed vessel *E*, and out again through the cork; and on to a gauge *f*, and through a sparking tube *g* to a mercury pump. The stop-cock *n* being still closed, the whole of the apparatus between *n* and the pump, including the vessel *D*, was exhausted, and liquid hydrogen introduced into *E*. The three-way cock *d* was then turned so as to connect *b* with *D*, and close *e*, and then *n* opened. *B* was thereby put in communication with *D*, which was at a

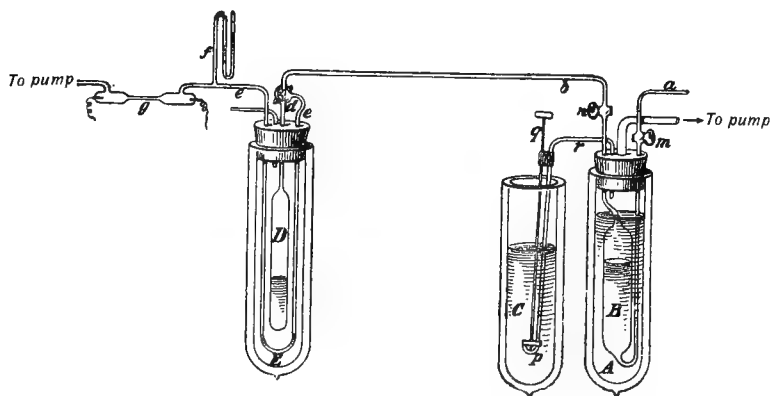


FIG. 1.

still lower temperature than *B*, and the gas dissolved in the liquid in *B*, along with some of the most volatile part of that liquid, distilled over, and the latter condensed in a solid form in *D*. When a small fraction of the liquid in *B* had thus distilled, the stop-cock *d* was turned so as to close the communication between *D* and *b*, and open that between *D* and *e*. Gas from *D* passed into the vacuous tubes, but in so doing it had to pass through the portion of *e* which was immersed in liquid hydrogen, so that condensable matter carried forward by the stream of gas was frozen out.

For separating the least volatile part of the gases, the vessel *E*, with its contents, was dispensed with, and the tube *b* made to communicate directly with that connected with the gauge, sparking tube, and pump; and generally several sparking tubes were interposed between the gauge

and pump, so that they could be sealed off successively. The bulk of the liquid in *B* consisted of nitrogen and oxygen. These were allowed gradually to evaporate, the temperature of *B* being still kept low so as to check the evaporation of the gases less volatile than oxygen. When a great part of the nitrogen and oxygen had thus been removed, the stop-cock *n* was closed, and the tubes partially exhausted by the pump, electric sparks passed through *g*, and the gases examined spectroscopically. More gas was then evaporated from *B*, and the spectroscopic examination repeated from time to time.

The general sequence of spectra, omitting those of nitrogen, hydrogen, and compounds of carbon, which were never entirely removed by the process of distillation alone, was as follows: The spectrum of argon was first noticed, and then as the distillation proceeded the brightest rays, green and yellow, of krypton appeared, and then the intensity of the argon spectrum waned, and it gave way to that of krypton until, as predicted by Runge, when a Leyden jar was in the circuit, the capillary part of the sparking tube had a magnificent blue colour, while the wide ends were bright pale yellow. Without a jar the tube was nearly white in the capillary part, and yellow about the poles. As the distillation proceeded, the temperature of the vessel containing the residue of liquid air being allowed to rise slowly, the brightest of the xenon rays began to appear, namely, the green rays about λ 5420, 5292, and 4922, and then the krypton rays soon died out and were superseded by the xenon rays. At this stage the capillary part of the sparking tube is, with a jar in circuit, a brilliant green; and is still green, though less brilliant, without the jar. The xenon formed the final fraction distilled.

Subsequently an improved form of apparatus was used for the fractionation. It is represented in fig. 2. A gas-holder containing the gases to be separated, that is to say the least volatile part of atmospheric air, was connected with the apparatus by the tube *a*, furnished with a stop-cock *c*. This tube passed on to the bulb *B*, which in turn communicated through the tube *b* and stop-cock *d* with a sparking tube, and so on through the tube *e*, with a mercurial pump. Stop-cock *d* being closed and *c* opened, gas from the holder was allowed to pass into *B*, maintained at low temperature, and there condensed in the solid form. Stop-cock *c* was then closed and *d* opened, and gas from *B* allowed to pass into the exhausted tubes between *B* and the pump. The tube *e* was partly immersed in liquid air in order to condense vapour of mercury, which would otherwise pass from the pump into the sparking tube. The gas passing into the sparking tube would, of course, have a pressure corresponding to the temperature of *B*, and this was further ensured by making the connecting tube pass through the liquid in which *B* was immersed. The success of the operation of separating all the gases which occur in air and which boil

at different temperatures depends on keeping the temperature of B as low as possible, as will be seen from the following consideration:—

The pressure p , of a gas G , above the same material in the liquid state, at temperature T , is given (approximately) by the formula

$$\log p = A - \frac{B}{T},$$

where A and B are constants for the same material. For some other gas G_1 the formula will be

$$\log p_1 = A_1 - \frac{B_1}{T},$$

and

$$\log \frac{p}{p_1} = A - A_1 + \frac{B_1 - B}{T}.$$

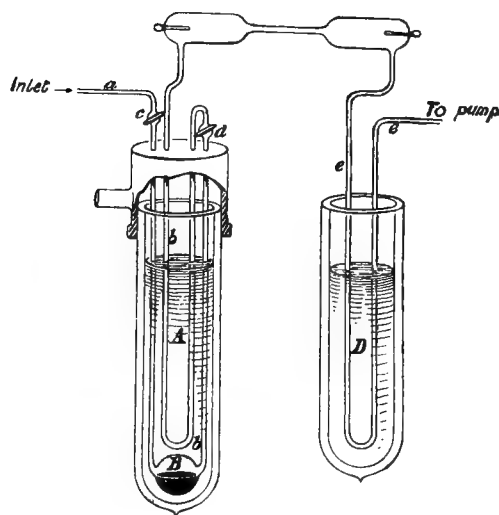


FIG. 2.

Now for argon, krypton, and xenon respectively the values of A are 6.782, 6.972, and 6.963, and those of B are 339, 496.3, and 669.2; so that for these substances and many others $A - A_1$ is always a small quantity, while $\frac{B_1 - B}{T}$ is considerable and increases as T diminishes. Hence the ratio of p to p_1 increases rapidly as T diminishes, and by evaporating the gases always from the solid state and keeping the solid at as low a temperature as possible, the gas first removable at the lowest pressure consists in by far the greatest part of that which has the lowest boiling point, which in this case is nitrogen, and is succeeded, with comparative abruptness, by the gas which has the next higher boiling point. By this method the

nitrogen and oxygen are removed without the necessity of sparking or absorption. The change from one gas to another is easily detected by examining the spectrum in the sparking tube, and the reservoirs into which the gases are pumped can be changed when the spectrum changes, and the fractions separately stored. Or, if several sparking tubes are interposed in such a way as to form parallel communications between the tubes *b* and *e*, any one of them can be sealed off at any desired stage of the fractionation.

The variation of the spectra of both xenon and krypton with variation in the character of the electric discharge is very striking, and has already been the subject of remark, in the case of krypton, by Runge, who has compared krypton with argon in its sensitiveness to changes in the electric discharge. Runge distinguishes krypton rays which are visible without a jar and those which are only visible with a jar discharge. The difference in the intensity of certain rays, according as the discharge is continuous or oscillatory, is no doubt very marked, but, with rare exceptions, we have found that the rays which are intensified by the oscillatory discharge can be seen with a continuous discharge when the slit of the spectroscope is wide. Runge used a grating, whereas we have, for the sake of more light, used a prism spectroscope throughout, and were therefore able to observe many more rays than he.

There is one very remarkable change in the xenon spectrum produced by the introduction of a jar into the circuit. Without the jar xenon gives two bright green rays at about λ 4917 and λ 4924, but on putting a jar into the circuit they are replaced by a single still stronger ray at about λ 4922*. In no other case have we noticed a change so striking as this on merely changing the character of the discharge. Changes of the spectrum by the introduction of a jar into the circuit are, however, the rule rather than the exception, and there are changes in the spectrum of krypton which seem to depend on other circumstances. In the course of our examination of many tubes filled with krypton in the manner above indicated, we have found some of them to give with no jar the green ray λ 5571, the yellow ray λ 5871, and the red ray λ 7600 very bright, while other rays are very few, and those few barely visible. Putting a jar into the circuit makes very little difference; the three rays above mentioned remain much the brightest, nearly, though not quite, so bright as before, and the blue rays, so conspicuous in other tubes, though strengthened by the use of the jar, are still very weak. In other tubes the extreme red ray is invisible, the rays at λ 5571 and 5871 absolutely, as well as relatively, much feebler, while the strong blue rays are bright, even brighter than the green and yellow rays above named. In one tube the blue rays could be seen, though not the

* This line is almost identical with a strong helium line, but the yellow line of helium was not seen.

others. This looks very much as if two different gases were involved, but we have not been able to assure ourselves of that. The case seems nearly parallel with that of hydrogen. There are some hydrogen tubes which shew the second spectrum of hydrogen very bright, and others which shew only the first spectrum; the second spectrum is enfeebled or extinguished by introducing a jar into the circuit, while the first spectrum is strengthened; and the conditions which determine the appearance of the ultra-violet series of hydrogen rays have not yet been satisfactorily made out.

It is to be noted that putting the jar out of circuit does not in general immediately reduce the brightness of the rays which are strengthened by the jar discharge. Their intensity fades gradually, and is generally revived, more or less, by reversing the direction of the current, but this revival gets less marked at each reversal until the intensity reaches its minimum. The rays strengthened by the jar discharge also sometimes appear bright, without a jar, on first passing the spark when the electrodes are cold, and fade when the electrodes get hot, reappearing when the tube has cooled again. Moreover, if the discharge be continued without a jar, the resistance in the krypton tubes increases rather rapidly, the tube becomes much less luminous and finally refuses to pass the spark. With an oscillatory discharge the passage of the spark and the brightness of the rays are much more persistent. This seems to point to some action at the electrodes, which is more marked in the case of krypton than in that of xenon.

The wave-lengths of the xenon and krypton rays in the tables below were determined, in the visible part of the spectrum, with a spectroscope having three white flint-glass prisms of 60° each, by reference to the spark spectrum of iron, except in the cases of the extreme red ray of krypton, which was referred to the flame spectrum of potassium, and its fainter neighbour, which we saw but did not measure. The indigo, violet, and ultra-violet rays were measured in photographs, taken with quartz lenses and two calcite prisms of 60° each. The spectrum of the iron spark was photographed at the same time as that of the tube, the former being admitted through one-half of the slit, and the latter through the other half.

The xenon spectrum is characterised by a group of four conspicuous orange rays of about equal intensities, a group of very bright green rays of which two are especially conspicuous, and several very bright blue rays. The only list of xenon rays we have seen is that published by Erdmann, with which our list does not present any close agreement except as to the strongest green lines. The number of xenon rays we have observed is very considerable, and some of them lie very near to rays of the second spectrum of hydrogen, but inasmuch as these rays are more conspicuous with a jar in circuit than without, which is not the character of the second spectrum of hydrogen, and, moreover, many of the brightest of the hydrogen

rays are absent from the spectrum of the tubes, we conclude that these rays are not due to hydrogen. Certain rays, which we have tabulated separately, have been as yet observed in only one tube: they include a very strong ultra-violet ray of unknown origin, and either due to some substance other than xenon, or to some condition of the tube which has not been repeated in the other tubes.

Our krypton rays agree much more closely with Runge's list, but outnumber his very considerably, as might be expected when prisms were used instead of a grating. Prisms, of course, cannot compete with gratings in the accuracy of wave-length determinations. We think that the krypton used by Runge must have contained some xenon, and that the rays for which he gives the wave-lengths 5419·38, 5292·37, and 4844·58 were really due to xenon, as they are three of the strongest rays emitted by our xenon tubes, and are weak in, and in some cases absent from, the spectra of our krypton tubes.

Our thanks are due to Mr R. Lennox, to whose skill in manipulation we are much indebted.

Tables of the approximate Wave-lengths of Xenon and Krypton Rays.

Rays observed only with a Leyden jar in circuit have an * prefixed, those observed only when no Leyden jar was in circuit have a † prefixed.

The intensities indicated are approximately those of the rays when a jar is in circuit, except in the case of the two rays to which a † is prefixed, which are not seen when a jar is in circuit. Rays which are equally intense whether a jar is in circuit or not have a || prefixed to the number indicating their intensities; those which are less intense with a jar than without have a < prefixed to the number expressing their intensities. The rest are, in general, decidedly more intense with a jar than without.

Xenon Rays.

Wave-lengths	Inten-sity	Wave-lengths	Inten-sity	Wave-lengths	Inten-sity	Wave-lengths	Inten-sity
*6596	4	6181	1	5895	1	5700	6
* 14	1	66	1	76	1	5668	4
6472	1	6097	6	56	1	60	1
6358	1	51	6	25	2	17	—
45	3	36	5	17	—	09	1
20	1	5976	6	5777	4	5583	1
02	1	72	—	59	4	73	1
6278	3	46	2	51	5	32	4
71	3	35	< 1	27	4	5473	3
6183	1	06	1	20	4	61	3

Xenon Rays—*continued*.

Wave-lengths	Intensity	Wave-lengths	Intensity	Wave-lengths	Intensity	Wave-lengths	Intensity
*5451	1	4634	2	4163	3	3824	1
39	3	24	<2	59	3	15	1
20	10	16	3	46	3	11	3
5372	6	02	8	42	1	07	1
* 68	1	4592	3	32	2	01	1
39	6	86	5	21	1	3792	1
13	1	77	3	12	2	87	1
09	1	56	2	09	6	83	1
5292	10	45	3	06	3	81	6
62	2	41	3	00	2	76	3
60	2	35	2	4099	3	73	1
40	—	25	5	93	1	70	1
27	1	22	1	79	<1	66	1
02	1	00	1	74	1	63	2
5192	6	4486	1	60	1	62	1
89	3	81	5	58	6	57	1
85	3	71	2	50	6	46	3
79	3	62	10	44	1	37	1
26	3	49	6	43	1	31	2
23	1	40	1	37	6	21	2
07	3	34	2	29	1	17	3
5080	2	15	8	25	3	12	2
68	5	07	3	21	1	08	1
52	1	4396	4	02	3	3689	1
45	6	93	4	3994	2	77	3
25	<1	86	3	91	3	73	2
4988	4	75	4	86	1	64	1
72	2	69	4	81	1	62	2
+ 24	+4	56	1	75	1	58	1
* 22	8	43	1	73	2	55	2
+ 17	+4	37	3	57	1	50	1
4890	3	31	10	55	4	45	6
87	—	22	3	51	<6	41	2
84	4	11	3	44	3	32	2
83	—	4297	3	39	1	24	10
76	4	86	3	26	1	16	1
44	10	72	3	23	6	13	4
30	1	69	3	15	1	10	2
23	3	63	2	08	4	07	4
* 18	3	51	3	06	1	02	1
07	<1	45	10	03	1	3597	3
4793	1	39	8	3894	3	84	8
87	2	27	1	85	3	80	8
79	2	23	5	80	3	65	4
69	2	15	10	77	3	56	3
40	1	14	6	70	2	53	5
34	<1	09	8	62	2	43	6
31	1	04	1	58	2	23	4
23	1	01	1	55	1	10	2
14	1	4198	1	50	2	04	1
4698	3	93	6	49	1	01	4
4677	band of close lines	81	10	42	4	3468	2
to		76	1	29	1	61	1
4668		72	1	26	1	54	1
52	4						

Wave-lengths of rays of unknown origin observed in the spectrum of one tube containing xenon but not present in the spectrum of other tubes:—

Wave-lengths	Intensity	Wave-lengths	Intensity
4589	—	3890	1
4071	1	72	1
67	1	3797	5
63	—	41	4
11	1	3684	10
3998	1	3573	2

Krypton Rays.

Wave-lengths	Intensity	Wave-lengths	Intensity	Wave-lengths	Intensity	Wave-lengths	Intensity
7600	8	5483	1	4812	3	4318	3
†7587	2	46	2	4766	10	01	7
6771	1	29	1	63	3	4293	10
6578	1	24	1	39	10	83	3
42	3	03	1	4694	3	74	4
11	2	5319	1	80	5	69	3
6487	3	05	1	59	8	60	1
58	<1	5278	1	50	1	56	1
51	3	29	1	35	6	51	5
20	<4	18	1	20	8	37	4
6305	3	15	1	15	6	4185	3
6170	2	* 09	5	10	3	72	1
6095	1	03	1	4598	1	45	8
82	1	5186	1	93	2	40	2
56	2	72	1	83	4	4119	3
21	1	66	5	77	8	09	6
11	2	43	4	25	3	4099	8
5992	3	26	6	05	2	89	8
5873	1	5087	3	4490	2	65	7
71	<10	78	1	75	6	58	6
5771	2	73	2	64	3 pairs	45	4
53	2	57	3	54	1	38	2
5690	5	34	1	37	6	08	2
82	5	23	4	32	6	05	1
50	1	14	2	23	2	3997	3
32	2	4980	1	00	1	94	6
5571	<10	60	1	4387	3	88	2
63	3	46	1	76	3	65	1
53	1	03	2	63	2	55	2
44	1	4847	2	56	12	39	1
23	2	45	2	23	2	28	3
06	2	* 33	5	20	8	21	8
00	2	26	3	19	3	18	2

† This is taken from Runge's number for the wave-length, omitting the fraction.

Krypton Rays—*continued.*

Wave-lengths	Inten-sity	Wave-lengths	Inten-sity	Wave-lengths	Inten-sity	Wave-lengths	Inten-sity
3913	6	3817	2	3719	10	3632	10
07	6	06	2	15	1	24	1
01	1	05	3	3691	1	08	6
3896	3	3784	10	87	5	00	6
76	7	79	8	81	7	3590	3
62	1	72	4	70	7	74	1
59	1	59	2	67	1	54	2
58	1	55	6	64	3	45	6
47	1	46	6	61	3	03	2
44	2	42	6	54	10	3489	2
42	1	36	3	49	3	70	1
39	1	34	4	38	4	60	3
37	2	22	5				

PROBLEMS OF THE ATMOSPHERE

[*Proceedings of the Royal Institution*, Vol. XVII. (1902), pp. 223 sqq.]

THE present liquid ocean, neglecting everything for the moment but the water, was at a previous period of the earth's history part of the atmosphere, and its condensation has been brought about by the gradual cooling of the earth's surface. This resulting ocean is subjected to the pressure of the remaining uncondensed gases, which for the present we may regard as composed solely of nitrogen and oxygen, and as these are slightly soluble they dissolve to some extent in the liquid. The gases in solution can be taken out by distillation or by exhausting the water, and if we compare their volume with the volume of the water as steam, we should find about 1 volume of air in 60,000 volumes of steam. This would then be about the rough proportion of the relatively permanent gas to condensable gas which existed in the case of the vaporised ocean.

Now let us assume the surface of the earth gradually cooled to some 200 degrees below the freezing-point; then, after all the present ocean was frozen, and the climate became three times more intense than any arctic frost, a new ocean of liquid air would appear about thirty-five feet deep, covering the entire surface of the frozen globe.

We may now apply the same reasoning to the liquid air ocean that we formerly did to the water one, and this would lead us to anticipate that it might contain in solution some gases that may be far less condensable than the chief constituents of the fluid. In order to separate them we must imitate the method of taking the gases out of water.

If a sample of liquid air cooled in the lowest temperature that can be reached by its own evaporation was connected by a pipe to a condenser cooled in liquid hydrogen, the result would be rapid distillation, and any volatile gases present in solution would distil over with the first portions of the air, and while the nitrogen and oxygen solidified in the condenser they could be pumped off, being still gaseous at the temperature of 20° absolute. A diagram of the apparatus is given in my lecture entitled "Gases at the

beginning and end of the century*." In this way, a gas mixture, containing, of the known gases, free hydrogen, helium and neon, has been separated from liquid air.

It is interesting to note in passing that the relative volatilities of water and oxygen are in the same ratio as those of the liquid air and hydrogen, so that the analogy between the ocean of water and that of liquid air has another suggestive parallel. The total uncondensable gas separated in this way amounts to about $\frac{1}{50000}$ th of the volume of the air, which is about the same proportion as the air dissolved in water.

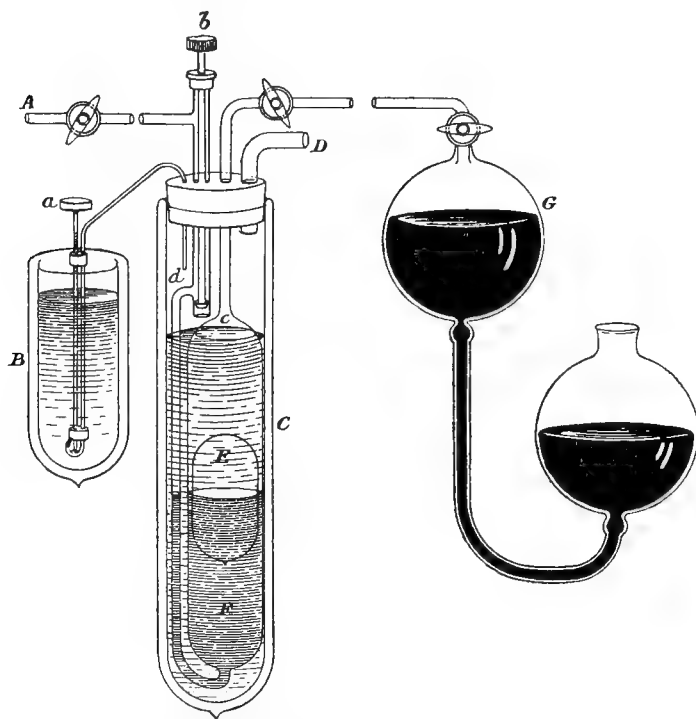
That free hydrogen exists in air in small amount is conclusively proved, but the actual proportion found by the process described above is very much smaller than Gautier has estimated by the combustion method. The recent experiments of Lord Rayleigh shew that air does not contain more than $\frac{1}{30000}$ th, so that Gautier, who estimated the hydrogen present as $\frac{1}{5000}$ th, has in some way produced more hydrogen than can be extracted from air by a repetition of the same process conducted by an equally competent experimenter.

The more volatile gases, helium, hydrogen and neon, can be separated from liquid air without the use of liquid hydrogen. For this purpose the arrangement of apparatus shewn in the figure overleaf is employed; the primary object being to liquefy air uncontaminated by compression pumps or the use of chemical reagents, at the pressure of the atmosphere, by cooling a vessel shaped like *F* to some -210°C . by the evaporation *in vacuo* of liquid air covering its exterior.

This is effected by connecting the tube *D* to a large air pump and regulating a supply of liquid air from the vessel *B* by means of the valve *a*. The external air freed from moisture by preliminary cooling on its way to the apparatus, is brought from the roof of the laboratory through glass pipes to the tube *A*, with its regulating stop-cock. It rapidly liquefies and begins to fill up the vessel *F*, which has a capacity of about 130 c.c., while the more volatile gases diffuse into the space above the liquid. In order to prevent their re-solution a very light and rather tight-fitting glass cylinder, shewn in *E*, is used as a float to diminish the liquid surface. As the liquid air accumulates the float *E* rises in the vessel *F*, until finally a small amount of uncondensed gas is left at *c*. The external supply of liquid air to *F* being shut off by closing the stop-cock *A*, the valve *b* connected with the tube *d* coming from the interior vessel *F* is opened. This discharges all the air which had been liquefied in *F* directly to its outside; thereby diminishing the amount required to be supplied from the vessel *B* for the next operation of filling *F*,

* *Proceedings of the Royal Institution*, Vol. xvi, p. 736.

and the float *E* falls to the bottom of the vessel. During this emptying of the vessel the separated gas expands and fills the whole of *F* under the given conditions of temperature and pressure. Care is taken, however, to leave a layer of liquid air below the float to guard against the gaseous contents in *F* being taken away in part by the air pump. The valve *b* is now shut again and *A* opened so that the operation of filling may be repeated, and after five or six sequences of this kind the accumulated gas in *F* is drawn off into a mercury receiver *G*. The total volume of gas collected in this way amounted to about $\frac{1}{35000}$ th of the volume of the air directly liquefied, and contained 38 per cent. of nitrogen, 4 per cent. of hydrogen, and 58 per cent. of mixed



helium and neon. On the average some 25 c.c. of gas were collected for every litre of liquid air produced, and as the apparatus works almost automatically, the method becomes a practical one for the separation of the most incondensable constituents of the atmosphere. After the removal of the hydrogen and nitrogen by sparking in the usual way with excess of oxygen over alkali, the helium and neon can be separated. This is easily done by freezing out the neon by passing the gaseous mixture through a tube cooled in liquid hydrogen; or the alternative method of spectroscopic fractionation described in a former lecture may be adopted to effect the general separation of all the constituents. The execution of the process on the larger scale will

enable gases other than helium and neon to be detected and ultimately separated.

A similar sample of gas collected from air that had been passed through lead pipes and dried with strong sulphuric acid contained about 33 per cent. of hydrogen, instead of the 4 per cent. found as above, or say at the most $\frac{1}{100000}$ th of free hydrogen in the original sample of air. The increased proportion of hydrogen must have originated from the contact of metal with water and acid vapours.

The total volume of the very volatile gases, helium and neon, collected in this way amounted to $\frac{1}{58000}$ th of the original volume of the air. This mixed gas had a density of 8.7 times that of hydrogen, so that the mixture was composed of 16 per cent. of helium and 84 per cent. of neon; if the latter be taken as having a density of 10. Thus air contains five times more neon than helium. These experiments prove that air contains as a minimum $\frac{1}{382000}$ th of its volume of helium, about $\frac{1}{70000}$ th of neon, and not more than $\frac{1}{100000}$ th of free hydrogen. In order to make the method strictly quantitative, the correction factor for solubility of these gases under the conditions of the experiment in the liquid air would require to be known. With the use of air freed from the volatile gases by liquefaction and standing for a day or two, the method was proved to be capable of detecting the presence of $\frac{1}{50000}$ th of free hydrogen in a specially prepared mixture. In a mixture containing $\frac{1}{5000}$ th of free hydrogen the loss from solubility, etc., amounted to about 50 per cent.

The spectroscopic examination of these gases throws new light upon the question of the aurora and the nature of the upper air. On passing electric discharges through the tubes containing the most volatile of the atmospheric gases, they glow with a bright orange light, which is especially marked at the negative pole. The spectroscope shews that this light consists, in the visible part of the spectrum, chiefly of a succession of strong rays in the red, orange and yellow, attributed to hydrogen, helium and neon. Besides these, a vast number of rays, generally less brilliant, are distributed through the whole length of the visible spectrum. The greater part of these rays are of, as yet, unknown origin. The violet and ultra-violet part of the spectrum rivals in strength that of the red and yellow rays. As these gases probably include some of the gases that pervade interplanetary space, search was made for the prominent nebular, coronal and auroral lines. No definite lines agreeing with the nebular spectrum could be found, but many lines occurred closely coincident with the coronal and auroral spectrum. But before discussing the spectroscopic problem, it will be necessary to consider the nature and condition of the upper air.

According to the old law of Dalton, supported by the modern dynamical theory of gases, each constituent of the atmosphere while acted upon by the

force of gravity forms a separate atmosphere, completely independent, except as to temperature, of the others, and the relations between the common temperature and the pressure and altitude for each specific atmosphere can be definitely expressed.

If we assume the altitude and temperature known, then the pressure can be ascertained for the same height in the case of each of the gaseous constituents, and in this way the percentage composition of the atmosphere at that place may be deduced.

Suppose we start with a surface atmosphere having the composition of our air, only containing $\frac{2}{10000}$ ths of hydrogen; then at thirty-seven miles, if a sample could be procured for analysis, we believe that it would be found to contain 12 per cent. of hydrogen and only 10 per cent. of oxygen. The carbonic acid practically disappears; and by the time we reach forty-seven miles, where the temperature is *minus* 132 degrees, assuming a gradient of 3.2 degrees per mile, the nitrogen and oxygen have so thinned out that the only constituent of the upper air which is left is hydrogen. If the gradient of temperature were doubled, the elimination of the nitrogen and oxygen would take place by the time thirty-seven miles was reached, with a temperature of *minus* 220 degrees.

The theoretical distribution of the chief components of our atmosphere, on the assumption of steady equilibrium, is graphically represented in Diagrams I and II. In the diagrams nitrogen, oxygen, hydrogen, argon, and carbonic acid are distinguished by several hatchings as thereon indicated. A horizontal line drawn across the diagram at any height marked in kilometres (0.62 mile) shews the percentage by volume of the constituents at that elevation by the respective lengths of line in the area of the individual constituents. The results of Hinrich's calculations, which involve no consideration of the effects of temperature, are represented in Diagram I, and those of Ferrel, who assumes a temperature gradient of 4° per kilometre, throughout the upper air, in Diagram II. The steeper the assumed temperature gradient the lower the elevation at which the nitrogen and oxygen are eliminated and the true hydrogen atmosphere begins. The elevations marked A, B, C and D in the diagram refer to the respective gradients of 4°, 3°, 2° and 1° per kilometre, and mark the end of nitrogen or the beginning of the true hydrogen atmosphere. The position A corresponds to 60 kilometres and a temperature of -220° ; B to 67 kilometres and -181° ; C to 76 kilometres and -132° ; and D to 87 kilometres and -67° .

On any of these temperature gradient hypotheses it appears that practically above 56 miles the atmosphere would be substantially composed of hydrogen. If helium and neon had been included in the calculations they

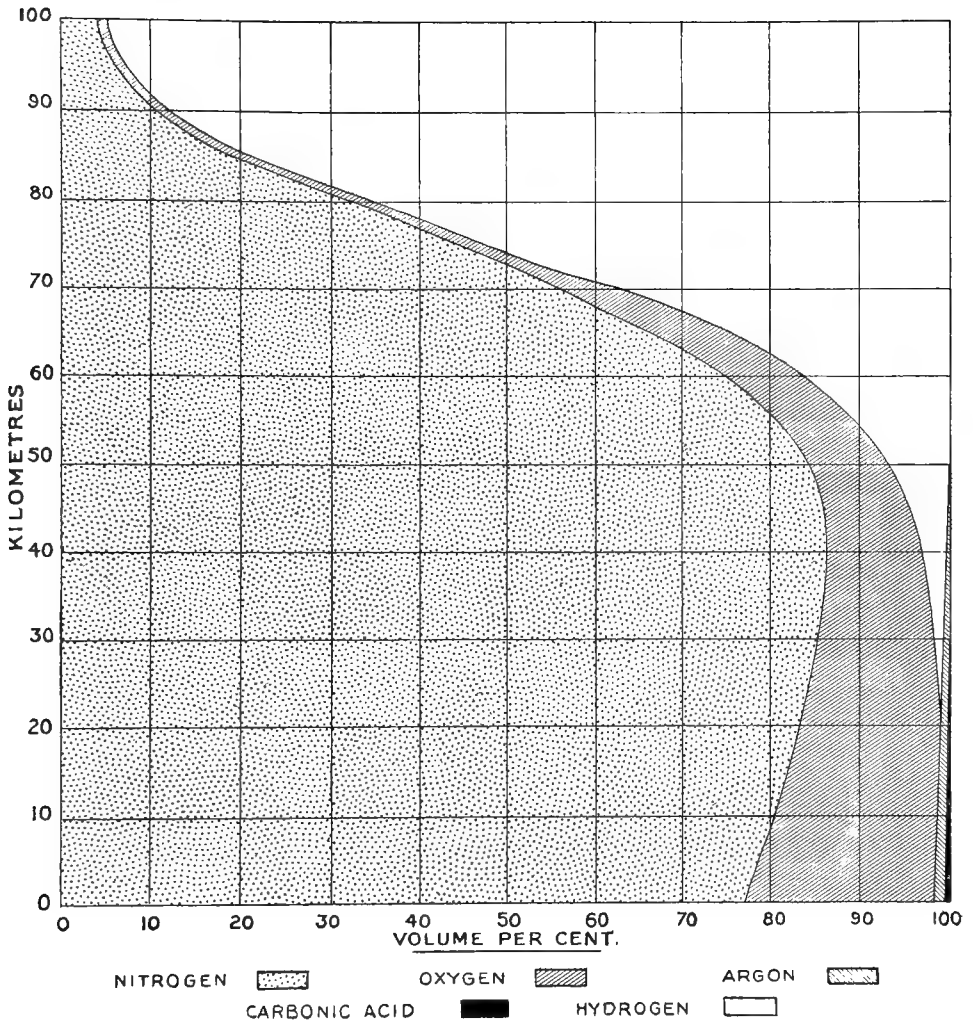


DIAGRAM I.

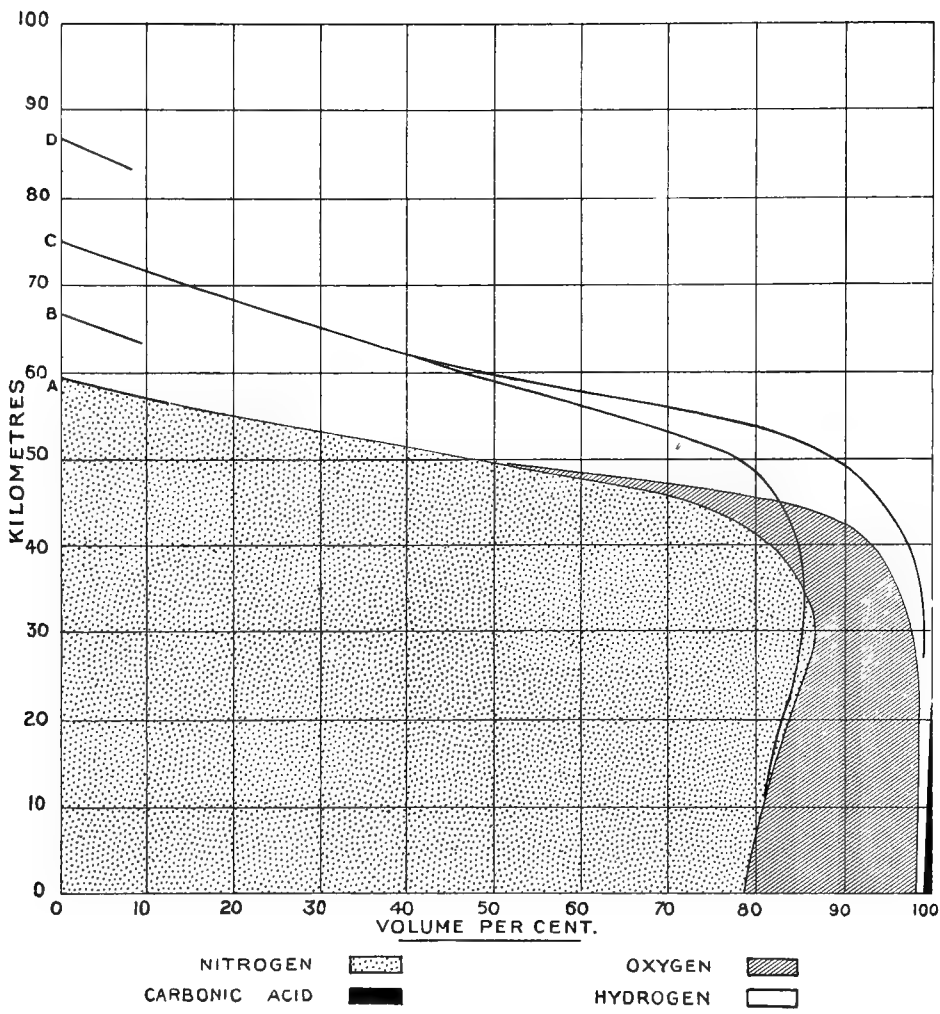


DIAGRAM II.

would have been found concentrated at high elevation between the regions occupied respectively by the hydrogen and the nitrogen in the diagrams. If the temperature is taken as constant, Diagram I shews that at an elevation of some 62 miles the composition of a sample of the air, if it could be secured, would be 95.1 per cent. of hydrogen, 4.6 per cent. of nitrogen, and 0.3 per cent. of oxygen.

The permanence of the composition of the air at the highest altitudes, as deduced from the basis of the dynamical theory of gases, has been discussed by Stoney, Bryan, and others. It would appear that there is a consensus of opinion that the rate at which gases like hydrogen and helium could escape from the earth's atmosphere would be excessively slow. Considering that to compensate any such loss the same gases are being supplied by actions taking place in the crust of the earth, we may safely regard them as necessarily permanent constituents of the upper air.

The temperature at the elevations we have been discussing would not be sufficient to cause any liquefaction of the nitrogen and oxygen, on account of the pressure being so low. If we assume the mean temperature as about the boiling-point of oxygen, then a considerable amount of the carbonic acid must solidify as a mist, if the air from a lower level be cooled to this temperature; and the same result might take place with other gases of relatively small volatility which occur in air. The temperature of the upper air must be above that on the vapour pressure curve corresponding to the barometric pressure of the locality, otherwise liquid condensation must take place. In other words, the temperature must be above the dew-point of air at that place. At very high elevations, on any reasonable assumption of temperature distribution, we inevitably reach a temperature where the air would condense, just as Fourier and Poisson supposed it would, unless the temperature is arrested in some way from approaching the zero.

Both ultra-violet absorption and the prevalence of electric storms may have something to do with the maintenance of a higher mean temperature than we should anticipate, following the deductions of our assumed formulas for temperature decrements. The whole mass of the air above 40 miles is not more than $\frac{1}{700}$ th part of the total mass of the atmosphere, so that any rain or snow of liquid or solid air, if it did occur, would necessarily be of a very tenuous description. In any case, the dense gases tend to accumulate in the lower strata, and the lighter ones to predominate at the higher altitudes, always assuming a steady state of equilibrium has been reached.

It must be observed, however, that a sample of air taken at an elevation of 9 miles has shewn no difference in composition from that at the ground, whereas, according to our hypothesis, the oxygen ought to have been diminished to 17 per cent., and the carbonic acid should also have become

much less. This can only be explained by assuming that a large intermixture of different layers of the atmosphere is still taking place at this elevation. This is confirmed by a study of the motions of clouds about six miles high, which reveals an average velocity of the air currents of some seventy miles an hour; such violent winds must be the means of causing the intermingling of different atmospheric strata. Some clouds, however, during hot and thundery weather, have been seen to reach an elevation of seventeen miles, so that we have direct proof that on occasion the lower layers of atmosphere are carried to a great elevation.

The existence of an atmosphere at more than a hundred miles above the surface of the earth is revealed to us by the phenomenon of twilight and the luminosity of meteors and fireballs. When we can take photographs of meteoric spectra, a great deal may be learnt about the composition of the upper air. In the meantime Pickering's solitary spectrum of a meteor reveals an atmosphere of hydrogen and helium, and so far this is a corroboration of the doctrine we have been discussing. It has long been recognised that the aurora is the result of electric discharges within the limits of the earth's atmosphere, but it was difficult to understand why its spectrum should be so entirely different from anything which could be produced artificially by electric discharges through rarefied air at the surface of the earth. Rand Capron, in 1879, after collecting all the recorded observations, was able to enumerate no more than nine auroral rays, of which but one could with any probability be identified with rays emitted by atmospheric air under electric discharge. Vogel attributed this want of agreement between nature and experiment, in a vague way, to difference of temperature and pressure; and Zöllner thought the auroral spectrum to be one of a different order, in the sense in which the line and band spectra of nitrogen are said to be of different orders.

Such statements were merely confessions of ignorance. But since that time observations of the spectra of auroras have been greatly multiplied, chiefly through the Swedish and Danish Polar Expeditions. The spectrum recorded on the ultra-violet side has been greatly extended by the use of photography, so that, in a recent discussion of the results, M. Henri Stassano is able to enumerate upwards of one hundred auroral rays, of which the wave-length is more or less approximately known. Of this large number of rays he is able to identify, within the probable limits of errors of observation, about two-thirds as rays which Professor Liveing and myself have observed to be emitted by the most volatile gases of atmospheric air unliquefiable at the temperature of liquid hydrogen. Most of the remainder he ascribes to argon, and some might, with more probability, have been identified with krypton or xenon.

The rosy tint often seen in auroras, particularly in the streamers, appears

to be due mainly to neon, of which the spectrum is remarkably rich in red and orange rays. One or two neon rays are amongst those most frequently observed, while the red ray of hydrogen and one red ray of krypton have been noticed only once. The predominance of neon is not suprising, seeing that from its relatively greater proportion in air and its low density it must tend to concentrate at higher elevations.

So large a number of probable identifications warrants the belief that we may yet be able to reproduce in our laboratories the auroral spectrum in its entirety. It is true that we have still to account for the appearance of some, and the absence of other, rays of the newly discovered gases, which in the way in which we stimulate them appear to be equally brilliant, and for the absence, with one doubtful exception, of all the rays of nitrogen. If we cannot give the reason of this, it is because we do not know the mechanism of luminescence—nor even whether the particles which carry the electricity are themselves luminous, or whether they only produce stresses causing other particles which encounter them to vibrate—yet we are certain that an electric discharge in a highly rarefied mixture of gases lights one element and not another, in a way which, to our ignorance, seems capricious.

The Swedish North Polar Expedition concluded from a great number of trigonometrical measurements that the average above the ground of the base of the aurora was fifty kilometres (thirty-four miles) at Cape Thorsden, Spitsbergen; at this height the pressure of the nitrogen of the atmosphere would be only about one-tenth of a millimetre, and Moissan and Deslandres have found that in atmospheric air at pressures less than one millimetre the rays of nitrogen and oxygen fade and are replaced by those of argon and by five new rays which Stassano identifies with rays of the more volatile gases measured by us. Also Collie and Ramsay's observations on the distance to which electrical discharges of equal potential traverse different gases throw much light on the question. They find that, while for helium and neon this distance is from 250 to 300 mm., for argon it is $45\frac{1}{2}$ mm., for hydrogen it is 39 mm., and for air and oxygen still less.

This indicates that a good deal depends on the very constitution of the gases themselves, and certainly helps us to understand why neon and argon, which exist in the atmosphere in larger proportions than helium, krypton, or xenon, should make their appearance in the spectrum of auroras almost to the exclusion of nitrogen and oxygen.

How much depends not only on the constitution, and it may be temperature, of the gases, but also on the character of the electric discharge, is evident from the difference between the spectra at the cathode and anode in different gases, notably in nitrogen and argon, and not less remarkably in the more volatile compounds of the atmosphere.

Without stopping to discuss that question, it is certain that changes in the character of the electric discharge produce definite changes in the spectra excited by them. It has long been known that, in many spectra, rays which are inconspicuous with an uncondensed electric discharge become very pronounced when a Leyden jar is in the circuit. This used to be ascribed to a higher temperature in this condensed spark, though measurements of that temperature have not borne out the explanation. Schuster and Hemsalech have shewn that these changes of spectra are in part due to the oscillatory character of the condenser discharge, which may be enhanced by self-induction, and the corresponding change of spectrum thereby made more pronounced.

If we turn to the question what is the cause of the electric discharges which are generally believed to occasion auroras, but of which little more has hitherto been known than that they are connected with sun-spots and solar eruptions, recent studies of electric discharges in high vacua, with which the names of Crookes, Röntgen, Lenard, and J. J. Thomson will always be associated, have opened the way for Arrhenius to suggest a definite and rational answer. He points out that the frequent disturbances which we know to occur in the sun must cause electric discharges in the sun's atmosphere far exceeding any that occur in that of the earth. These will be attended with an ionisation of the gases, and the negative ions will stream away through the outer atmosphere of the sun into the interplanetary space, becoming, as Wilson has shewn, nuclei of aggregation of condensable vapours and cosmic dust. The liquid and solid particles thus formed will be of various sizes; the larger will gravitate back to the sun, while those with diameters less than one and a half thousandths of a millimetre, but nevertheless greater than a wave-length of light, will, in accordance with Clerk-Maxwell's electromagnetic theory, be driven away from the sun by the incidence of the solar rays upon them, with velocities which may become enormous, until they meet other celestial bodies, or increase their dimensions by picking up more cosmic dust, or diminish them by evaporation. The earth will catch its share of such particles on the side which is turned towards the sun, and its upper atmosphere will thereby become negatively electrified until the potential of the charge reaches such a point that a discharge occurs, which will be repeated as more charged particles reach the earth.

ON THE PROBABLE PRESENCE IN THE SUN OF THE NEWLY DISCOVERED GASES OF THE EARTH'S ATMOSPHERE

[*Proceedings of the Cambridge Philosophical Society*,
Vol. XII. (1903), pp. 87 sqq.]

SOON after the publication of the list of wave-lengths of the rays which Professor Dewar and I found to be emitted by the most volatile gases of the atmosphere, Stassano pointed out that the bright rays of solar protuberances, of which the wave-lengths had been measured by Deslandres and Hale, agreed closely with rays in our list. The wave-lengths need to be determined with very great exactness in order to prove coincidence, and neither set of wave-lengths have, as yet, been measured with such nicety as that. Nevertheless the agreement is sufficient to make it probable that the same gases are concerned in the production of the rays in question.

When, in the *Astrophysical Journal*, Vol. xv, pp. 313 sqq., Humphreys published a list of wave-lengths of 339 bright rays of the chromosphere and corona, which he had photographed in Sumatra during the total eclipse of May, 1901, I compared this list with our list of the wave-lengths of rays of the most volatile atmospheric gases, and with those of xenon and krypton, which we had subsequently published, and with those of argon. The result was that of the 339 rays in Humphreys' list 209 do not differ in wave-length by more than one unit from rays emitted by gases of the earth's atmosphere. In our published lists the wave-lengths are given to four figures only in Rowland units, those of Humphreys' list are given to tenths of a unit, so that we are far from being able to prove coincidence in any case. Nevertheless it is so very probable that every gas which is in the earth's atmosphere is also in the sun's, and so much more likely that rays appearing in the chromosphere at a height of 9 seconds of arc, or 4000 miles, above the photosphere, should be due to gases of great volatility than to such metals as titanium or strontium, that it is much safer to treat the question as an open one, than to assume that titanium and other metals of high atomic weight are always present in the state of vapour at such a distance from the sun's surface, while much more volatile metals, such as sodium, are not regularly present at a quarter of that height.

We have been expecting from Mr Baly for a long time past a list of wave-lengths of the gases neon, krypton and xenon determined with great exactness by the use of a grating. The announcement that these measurements were in progress was made more than two years ago, and when the list appears we shall be in a better position to judge of the nearness of the coincidences. Meantime I have remeasured some of the rays of the most volatile gases, still, however, with only a prismatic spectroscope, so as to get, approximately, the fifth figure of the wave-length, and the result has been in many cases to bring my figures into closer agreement with those of Humphreys. The exactness of Humphreys' wave-lengths is quite as important a factor in the settlement of the question as that of mine. He obtained six photographs on celluloid films with a large concave grating of 30 feet focal length, used without any slit. The first had an exposure of 2 seconds immediately after second contact. Two seconds sufficed for a change of film, and then the second film was exposed for 5 seconds, and the third for 15 seconds, the fourth had a lengthened exposure of 2 minutes during the middle of totality, the fifth 15 seconds, and the sixth 8 seconds, ending 3 seconds before third contact. The dispersion of the spectrum was so great that one millimetre on the film corresponded to 3.66 Ångström units, and the range of the spectrum depicted extended from λ 3118 to λ 5204. The latter limit was probably determined by the want of sensitiveness of the films to lower green rays, for it would have been of great interest if the range had included the most characteristic rays of coronium, krypton, and neon. At the upper end the Fraunhofer line *S* is just excluded. This too is to be regretted, as *S* is a triple line of iron very unlikely to be reproduced by any mixture of elements excluding iron. The dispersion is ample for very exact determinations of wave-length if there were no difficulties in the way of exact measurement. Humphreys has met these difficulties as best he could, and I do not propose to discuss them now, but I may perhaps explain one or two of them. The station where the photographs were taken was near the northern limit of totality, so that the duration of totality was less than half what it was in the centre of the shadow. From these durations of totality I have calculated that the points of contact of the limbs of sun and moon were each nearly 63° from the diameter of the sun parallel to the line of the moon's apparent motion: and the instrument was so arranged that the ruling of the grating was parallel to that line, and in consequence the dispersion at right angles to that line, and the definition affected as little as possible by the moon's motion relative to the sun. During the exposures the tangents at the centres of the small arcs photographed would at first be inclined at about 27° to the direction of the moon's path and would gradually swing round until at mid totality they would be parallel to it, and then on until they were again inclined at about 27° to that direction, but on the opposite side. This motion tends to blur the definition of the arcs, but the effect would be very small on the 1st, 2nd, and 6th films,

and not great on the 3rd and 5th, but it would be very great on the 4th film for rays emitted only from parts of the chromosphere at much less distance than seven seconds of arc from the sun's limb. Rays emitted from the chromosphere at heights exceeding $7.3''$ would give arcs crossing the direction of dispersion at right angles, and would have well defined edges on the inside, unaffected by the moon's motion. There are however very few of such rays besides *H* and *K* and the strong hydrogen and helium rays.

The wave-lengths had to be determined by measuring the distances between the arcs on the films in the direction of dispersion and interpolating between such of the arcs as could be identified as due to rays of which the wave-lengths were well known. Rays answering to this test would be those above mentioned, namely, *H* and *K* and the strong rays of hydrogen and helium, and one or two very characteristic groups such as the *b* group of magnesium and, perhaps, the iron triplet 4046—4071. Indeed on looking through the list I do not see any ray other than these which I could identify with certainty without assuming it to be a reversal of a Fraunhofer line. Humphreys does not say which rays he used as fiducial rays between which he could interpolate. Those which I have just named seem to me too few, and too unequally distributed through the spectrum, to give very trustworthy wave-lengths in all parts of the spectrum. No scale of reference, made with artificial light and the same grating used without a slit, could well be made, or had in fact been attempted.

In his list Humphreys gives, against each chromospheric ray, the Fraunhofer line in Rowland's list which has the wave-length nearest to that found for the chromospheric ray. As there are 13,595 lines in Rowland's list in the range of the spectrum embraced by Humphreys' 339 lines it is not surprising that a Fraunhofer line is to be found for every one of Humphreys' lines, so close that the difference of wave-length is in most cases less than a tenth of a unit and rarely exceeds two-tenths. In discussing his results he evidently assumes the rays to be identical, and ascribes them to the metal (if any) indicated by Rowland. There are however some remarkable exceptions to this. They are the rays of helium, and the ultra-violet rays of hydrogen which do not appear as Fraunhofer lines. He does not hesitate to ascribe 4 rays to helium and 24 others to hydrogen in preference to identifying them with the nearest Fraunhofer lines. And I think he is right in so doing, notwithstanding the fact that several of these rays have never been observed to be emitted by hydrogen, have not been seen in the spectrum of any star, and are believed to be due to hydrogen only because the wave-lengths found for them agree closely with the values found by calculation for the prolongation of the well known series of hydrogen rays.

It is a noteworthy fact, that whereas it is very difficult to get from a tube containing a residue of carefully purified hydrogen any rays of this series

above H_{ζ} , $\lambda 3889$, yet when the tubes contain sensible quantities of helium and neon, they readily give many lines of the series. Up to H_{π} , $\lambda 3691.5$, these rays give very long arcs on Humphreys' films and are therefore emitted from the upper layer of the chromosphere. Why the presence of helium and neon along with hydrogen should conduce to the development of this series I cannot guess, but whatever the cause it seems to prevail in the sun. Besides the four helium rays above mentioned, other three helium rays might well be identified with arcs on Humphreys' films; $\lambda 3613.78$ is much nearer in wave-length to Humphreys' ray $\lambda 3613.8$ than the scandium ray with which he identifies it; and $\lambda 4143.92$ is nearer to $\lambda 4144.0$ than the iron ray to which it is ascribed; and Humphreys' ray 3820.7 gives a very long arc on film IV, and is probably the rather strong helium ray $\lambda 3819.75$. There are two rays $\lambda 3388$ and $\lambda 3456.5$ giving arcs very long, broad and hazy, which Humphreys cannot distinguish by measurement from Fraunhofer lines ascribed to titanium, but doubts whether they are really due to that metal. We have found that the most volatile atmospheric gases, probably neon, give rays at about $\lambda 3388.8$ and $\lambda 3456.8$; the former is rather a strong ray, the latter a weak one. It is possible the solar rays may be identical with them.

That the same gases must be in the atmospheres of the sun and planets appears to me certain. The subject has been discussed by many, but some of them seem to have gone off the track in ascribing the diffusion of these atmospheres to those molecules which on the kinetic theory chance to acquire such a velocity as will carry them beyond the attraction of the planet with which they had been associated. Dr Bryan has calculated that if we suppose the earth's atmosphere to have a definite surface there is practically no probability that any appreciable amount, of even so volatile a gas as hydrogen, can escape with such velocity from that surface that it will not return, provided it be actuated only by the kinetic energy of the gas and by gravitation. Dr Bryan is careful to point out that other considerations may entirely alter the problem. Now the postulate of a definite surface to the earth's atmosphere and no gas to be encountered outside it cannot be conceded, nor can the motion of the earth in its orbit be left out of account. If we talk of a gas leaving the atmosphere we need define the limit of the atmosphere, and that is not easy. I do not think that it has any definite limit, but we may make an arbitrary one. Shall we say that when the density is reduced to $\frac{1}{10^{12}}$ of what it is at the earth's surface we have reached that limit? At all events I do not think there is any evidence that the density of the residuum of gas in planetary space is less than that. If we take Dr Bryan's figure (derived I think from Lord Kelvin) that the number of molecules in one cubic centimetre of gas at normal pressure and temperature is approximately 10^{21} , and suppose it reduced to $\frac{1}{10^{12}}$ of that, we shall still have 10^9

molecules left in each cubic centimetre, and a molecule running into such a crowd has as good a chance of being knocked further away as it has of getting back. In fact if we consider a layer of air at this density, one cubic centimetre thick, all round the earth, and remember that the free path is very long, even if we suppose that the molecules all have only the average kinetic energy due to their temperature, many of them will, in a small fraction of a second, have passed far into the layers outside, and it is an equal chance whether the same molecules get back, or others are knocked back instead of them. We do not know at all what the temperature of the residuum of gas in planetary space may be, but it is probably very different from that which a black body would assume if left there. The diffusion of each layer into those above and below it will go on, even at a low temperature, with rapidity; and though it is true that the layer will contain but an infinitesimal fraction of the earth's atmosphere, yet as it is diffused into neighbouring layers in a small fraction of a second, and there are more than 30 millions of seconds in a year, and the solar system has been many millions of years in settling into its present state, there has been time enough for some considerable interchange of the atmospheres of the sun and earth. It is, however, far more probable that the solar system has settled into its present state from a nearly uniform gaseous mass, than that the materials out of which the sun and planets have been aggregated should have been distributed in such a heterogeneous way as to give a marked distinction between the atmospheres. Nor can we suppose that the sun and planets can have licked up all the gases out of planetary space. For if we could suppose that, and the earth with its atmosphere moving through empty space, the incoherent atmosphere must, I suppose, distribute itself in a long trail throughout the earth's orbit, and this trail would rapidly diffuse into the void space, and the process of diffusion would go on until the amount lost by the earth in its course was counterbalanced by the amount licked up, in fact until gas at a certain average density was distributed throughout the whole of the space in which the earth circulates. That average density will be the same whether we suppose the earth to start with its atmosphere in void space, or to start with a less dense atmosphere in space filled with gas of greater density than that average. Also the distribution of the several gases which have molecules of different masses will ultimately be the same in these two cases. The proportion of gases of smaller molecular mass will increase outwards from the earth's surface as well as from that of the sun, and the interchange between the sun and earth will go on most quickly in the case of the gases of least molecular mass, or in fact those which are most volatile.

ON DIFFERENCES BETWEEN THE SPECTRA AT ANODE AND KATHODE IN CERTAIN GASES, AND ON THE PROBABLE REASONS FOR THESE DIFFERENCES

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Vol. XII. (1904), pp. 337 sqq.]

It is well known that the spectrum of the glow about the kathode, when a continuous electric discharge passes through rarefied gas, is, in some cases, different from that of the light emitted by the gas in other parts of the tube.

In the case of nitrogen both these spectra were carefully described by Ångström and Thalén in 1875*, and were distinguished by them from the, so-called, line spectrum, which is produced in nitrogen by a disruptive discharge. They noticed that the glow about the kathode increased, and became more brilliant, as the gas was more rarefied, but they attributed the light at the anode to an oxide of nitrogen. Another element well known to give two spectra in the same tube at reduced pressure is hydrogen†, but I am not aware that anyone hitherto has pointed out that these two spectra bear to each other a relation similar to that which subsists between the two channelled spectra of nitrogen, namely, that one, the series of rays corresponding to the Fraunhofer lines *C*, *F*, *G'*, *h* and Huggins' ultra-violet series, is that of the kathode glow, while the second spectrum, also consisting of lines, but much more numerous, is that of the anode. It is as easy to shew this as to shew the corresponding facts with regard to the spectra of nitrogen. To shew it clearly it is necessary to have the hydrogen as pure as possible. I have used hydrogen occluded in palladium which was enclosed in a glass tube fitted with a stop-cock, which may be called stop-cock (*a*). This tube, beyond (*a*), was sealed by fusion to a long and wide tube loosely filled with phosphoric anhydride, also having a stop-cock (*b*) at its farther end, beyond which it was sealed to the sparking tube, and this in turn to a mercury pump. Stop-cock (*b*) being open and (*a*) shut, the air in the system was exhausted as completely as the pump would do it. Stop-cock (*b*) was then closed and (*a*)

* "*Recherches sur les spectres des métalloïdes*," *Nova Acta Reg. Soc. Sc. Ups.*, Ser. III.

† Plücker and Hittorf, *Trans. R. S.*, 1865.

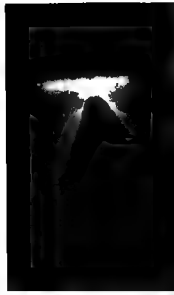


FIG. I.

Kathode glow in oxygen.
Kathode terminated by
two plane facets un-
equally inclined to the
axis.



FIG. II.

Kathode glow in oxygen.
Kathode terminated by
one plane facet in-
clined to the axis at an
acute angle.



FIG. III.

Kathode glow in hydrogen.
Kathode a six sided
prism, giving an end-
on view.

In Fig. III the central spot is the luminous sheath of the kathode, whence six fine rays diverge, and after crossing the dark space spread out forming the kathode glow, beyond which the bright spots are due to fluorescence of the glass tube.

opened to allow hydrogen from the palladium to fill the tube holding phosphoric anhydride, and then (*a*) was closed again. The whole was left in this state all night. Next morning on passing a spark the tube shewed the well known spectrum of carbon oxide, no doubt from some of that gas having escaped from the glass. This having been pumped out as much as possible, stop-cock (*b*) was opened and well dried hydrogen from the phosphoric anhydride tube allowed to enter the sparking tube, and then the whole system, up to stop-cock (*a*), again exhausted. Stop-cock (*b*) was then closed and (*a*) opened for a short time and then closed again. The system was then left until evening, when the same series of operations were repeated. It was not until the fifth day that the CO^2 ceased to appear in the sparking tube, so that I could observe the behaviour of the hydrogen alone. Even after such treatment the tubes generally give out more carbon oxide if kept for many days. Much sparking of the tube in a highly exhausted state must be avoided, because the sparking is likely to decompose the glass. If the yellow sodium light is seen at the point where the electrode enters the tube it is a sure sign of decomposition of the glass, and I could never get such tubes to give clean spectra.

With a fairly clean tube, still attached to the pump and to the other tubes, it is easy to trace the changes in the spectra of hydrogen at different pressures. At about 4 mm. pressure the negative glow is well seen about the kathode. It begins as a close-fitting pink sheath on the kathode, which expands as the pressure is reduced. The spectroscope shews that its light is chiefly that of the rays *C*, *F*, and *G'*. It maps out extremely well the course of the kathode rays. If the kathode be a cylindrical wire of one or two millimetres thickness, terminated by two plane facets inclined to the axis, the gas is lighted up equally all round the cylindrical part of the kathode, while from near the centre of each terminal facet proceeds a cone of luminosity exactly in the course of the kathode rays, see Figs. I, II, and when the density of the gas is so reduced that a sensible fraction of the kathode rays escapes absorption by the gas, the base of the cone, where it meets the glass, makes the tube fluoresce. If the kathode be a six-sided prism instead of a cylinder, and be looked at end on, six conical pencils of luminosity diverge from the plane faces of the prism and are easily traceable right across the Crookes dark space, which is only relatively dark; see Fig. III. It is well known that the luminosity is deflected by a magnet along with the kathode rays.

When the pressure of the gas is so far reduced that striations appear, the spectrum of the negative glow consists of the lines *C*, *F*, etc. only, without a trace of the second spectrum. In the light of the negative glow photographs shew nine of the ultra-violet lines of hydrogen. Turning the spectroscope on to the head of the first stria, the second spectrum is there easily visible, and so it is at the bright convex edge of succeeding striæ. In the capillary both spectra are bright at first, but as the pressure is reduced the lines *C*, *F*, etc.

become relatively brighter and the second spectrum weaker, until the latter entirely disappears from the capillary, and is seen only at the bright spot on the anode. At the higher pressures (7 mm.) the bright spot on the anode shews only the second spectrum without a trace of *C* or *F*. The behaviour of the two channelled spectra of nitrogen is precisely similar. When the dark space is sufficiently developed the kathode glow shews none of the brilliant channellings in the orange which are characteristic of the positive spectrum, but they appear plainly at the head of the first striation, and as the exhaustion proceeds are driven further and further from the kathode, until the capillary shews only the spectrum of the negative glow, and the orange and yellow channellings are seen only on the anode.

In order to see these appearances the discharge must be continuously in one direction, and therefore, if an induction coil be used, there must be sufficient resistance in the circuit to stop the passage of the indirect induced current. A short air gap will serve this purpose very well without making the discharge sensibly discontinuous. A condenser cannot be used in connexion with the secondary circuit, since it produces an oscillatory discharge.

Pure oxygen produces no luminous positive column and no striations, as was observed by Morren, and the whole of the light emitted by it in a tube at low pressure under the influence of a continuous electric discharge appears to be that of the negative glow. Schuster has carefully observed the spectrum of oxygen, but my observations, made with a continuous current from an induction coil giving a spark in air 7 cm. long, do not accord with his in all respects. In the first place I have failed to see the continuous spectrum and the narrow spark throughout the tube, when the exhaustion first reaches the stage at which the discharge will pass through the tube*. The first luminous indication of a discharge that I see is a thin sheath of luminosity around the kathode and nothing more. As the exhaustion proceeds the glow at the kathode spreads out, and in a darkened room a very faint orange-coloured light is seen in the capillary, but the rest of the tube is dark, and so is the anode if all carbon dioxide has been well removed. A trace of carbon dioxide shews itself by producing a slight whitish cloud on the anode, and is almost always seen after a time, so that it is only in a tube from which carbon dioxide has been well exhausted, and then only for a short time after being refilled with pure oxygen, that the anode shews no cloud. By further exhaustion the negative glow becomes more diffuse and in the capillary becomes quite bright. By still further exhaustion the negative glow is further diffused, the light of the capillary again pales, and the glass about the anode fluoresces under the action of the kathode rays which get through the capillary.

Schuster distinguishes the spectrum of the negative glow, which he

* "Spectrum of Metalloids," *Phil. Trans. R. S.*, Part 1, 1879, Exp. 8.

describes as consisting of five bands in the green and orange, from the four lines, which he calls the compound line spectrum. But I am quite unable to make out that these are two independent spectra. I always see both together in the negative glow and have never seen either produced in any other way. When the glow is very faint the three green bands are more easily seen than the lines because they fill a larger space on the retina, not because they are intrinsically brighter. And when the density of the gas is such that the dark space extends but a short distance round the kathode, both the bands and lines are very bright, brighter than they are in the capillary at any stage of the exhaustion.

Schuster's elementary line spectrum is best seen when the discharge is taken in oxygen at atmospheric pressure, nevertheless it is very well seen in the negative glow along with the bands and lines above mentioned, and can be easily photographed from that source.

I have reason to think that sulphur resembles oxygen in giving no anode light. Hitherto I have not been able to examine the discharge in sulphur vapour, but in sulphurous acid gas the kathode glow gives a series of bands which are probably those of sulphur, and are entirely absent from the anode which appears to have no spectrum.

Chlorine, Bromine, and Iodine closely resemble one another in their behaviour. Each gives a bright green negative glow, of which the spectrum consists of bright lines, described by Salet*, of which the groups in the green are most characteristic. The light from the anode seems to be only a continuous spectrum, very bright in the case of iodine and bromine, less bright in chlorine. In chlorine I see no lines at all in this continuous spectrum, which extends through the orange and green. In bromine, and iodine, the disappearance of the green lines at the anode is as well marked a feature as in chlorine, but the orange lines and some others are visible. Nevertheless I do not think that they belong to the anode, for a reason which is peculiar to the halogens so far as I have observed. When the pressure is not much less than that at which the spark will just pass through the gas, the path of the discharge forms a thread through the tube from one electrode to the other and there is no definite kathode glow, but the whole thread of discharge seems to emit kathode rays, for it makes the glass fluoresce exactly as if it were exposed to kathode rays. The spectrum of the thread of light also is that of the kathode glow superposed on the continuous spectrum of the anode. The fluorescence of the tube falls away when the pressure is reduced, and so does the brilliance of the light emitted, especially in the wide part of the tube, while the glow at the kathode becomes plainly developed; nevertheless I think the thread of discharge continues to emit kathode rays to some extent, and that the lines observed at the anode are really due to

* *Ann. Chimie et Physique* (4), xxviii, 24, 1873.

such rays. It is in accord with this supposition that bromine and iodine, which produce the strongest fluorescence, are also those which shew the lines at the anode.

It is difficult to manipulate the halogens because the mercury pump cannot be used directly, so that I had to reduce the pressure by connecting the sparking tube with a globe previously exhausted, and this involved the use of stop-cocks which had to be lubricated; and further the electrodes are rather rapidly attacked by halogens. I did not see striations in any one of the three substances, or well defined dark space.

Every metallic vapour, so far as I have yet observed, shews but one spectrum at both electrodes and throughout the tube.

Mercury, when a globule is made the kathode, shews a brilliant green negative glow at the surface of the metal, and a less bright patch of light where the kathode rays strike the surface of the metal when this is the anode. In both the spectrum is the same, with the well known green line, pair of yellow lines and indigo blue line, of mercury. When the tube is warmed to increase the pressure of the mercury vapour the glow which fills the tube shews the same spectrum, and there is no other spectrum at the anode nor is any definite positive column developed, or any striation.

Other metallic vapours examined were those of sodium, cadmium, and thallium. Plain tubes, without capillary, about 15 cm. long, enclosing fragments of the several metals, were pumped out, and, while still connected with the pump, were heated by gas jets, in a small furnace, built up of tiles from a combustion furnace, so that the whole tube was tolerably equably heated. Small openings left between the tiles allowed the spectrum to be observed. After the carbonic acid gas emitted by the glass had been pumped out as completely as possible, the tube and its contents were gradually heated, and though the pressure of the vapour could not be measured, it was varied by raising the temperature more or less.

The sodium vapour at very low pressure shewed its presence on passing the discharge by a long positive column with a well marked dark space about the kathode. The kathode glow was not strong but fairly well seen. At first the spectrum shewed lines of hydrogen as well as sodium, and the positive column shewed striation, but these disappeared when the hydrogen had been well pumped out. The light about the kathode then shewed only the *D* lines of sodium and a trace of the pair in the citron at about λ 568, while the bright column shewed in addition the pairs in the green and blue at about λ 515 and 498. The head of the bright column was concave to the kathode and was really the negative glow, separated from the kathode by a relatively dark space in which the spectrum was weak. There was no break in the column, and it was about equally bright quite up to the anode

and gave the same spectrum throughout. At a somewhat higher pressure of vapour the light about the kathode, and throughout the column, gave brightly, besides *D*, the pairs at about the wave-lengths 616, 568, 515, 498, 475, and 466. They were identified by comparison with the spectrum of the spark in air between two beads of sodium carbonate. The fragments of solid sodium, or rather the skin of oxide they had acquired before the tube was pumped out, fluoresced brilliantly in the kathode rays with an emerald green light, which however gave only a continuous spectrum.

With cadmium vapour, when all carbon dioxide had been pumped out, there was no striation. The spectrum was the same in all parts of the tube, and shewed the characteristic triplet, about λ 5085, 4799, 4677, the orange line about λ 6438, and the green line about λ 5153. At the kathode, when the vapour pressure was not too low, there appeared in addition the two green lines about λ 5378, 5337, and the indigo blue line about λ 4415, usually seen only with a jar discharge in the spark between cadmium electrodes in air. As these three lines were not observed at the anode it may be supposed that they belong exclusively to the kathode glow. I think, however, that as they are seen only at higher pressure when the absorption of the kathode rays is most rapid and the consequent intensity of the glow greatest, their appearance is a question of relative intensity, and they are not part of a different spectrum.

In thallium vapour there was a good negative glow which shewed the green thallium line only. The anode shewed the same. The whole tube was filled with a green glow, unstriated.

In this respect all the metals examined behaved alike.

Turning to compound gases. Hydrochloric acid gives no spectrum which I can ascribe to the undecomposed molecules. It gives, in a tube with platinum electrodes, a good kathode glow with a spectrum which consists of the lines of chlorine and the first spectrum of hydrogen, and nothing else that I can detect. The capillary shews in addition a continuous spectrum in the orange and green, due, I suppose, to chlorine; and the anode shews this continuous spectrum.

Striæ of a reddish tint, very faint and thin, are formed in succession close to the kathode and move slowly away from it, becoming more developed as they cross what would be the dark space if the head of the positive column were stationary. They were not bright enough to allow of my making sure that they shewed the second spectrum of hydrogen, but from their red tint I conclude that they are due to hydrogen. If so their gradual formation probably arises from decomposition of hydrochloric acid at the kathode. They move up to the anode and then disappear. This continuous movement implies some sort of circulation such as we may suppose to occur if the ions

of hydrochloric acid are dissociated in a strong electric field and are re-associated in a weak one. The continuous movement of the striæ, if we except a little flickering now and then, does not, so far as I have observed, occur except when there is reason to suppose that chemical change attends the discharge. For example, striæ are formed and move from kathode to anode in a mixture of cadmium vapour with carbonic acid gas, where probably the latter gas gives up half its oxygen to the metal in one part of the field, and the reverse reaction occurs in another part of the field.

The behaviour of water vapour was analogous to that of hydrochloric acid. When the carbonic acid gas had been thoroughly pumped out, and the pressure of the residual water vapour reduced to about one and a half millimetres by cooling a prolongation of the tube to -15°C ., there was a bright crimson kathode glow, a red capillary, and hardly any light on the anode. Platinum electrodes were used in this case. The kathode glow gave the first spectrum of hydrogen very bright, and much less brightly four lines in the blue, which by comparison with an oxygen tube I identified as oxygen lines. They were not easily seen at first, more easily after a little sparking. I looked for the orange and green lines of Schuster's compound line spectrum, but failed to detect them. Nor could I see the two broad green bands. The blue lines were, however, observed and compared with the oxygen lines several times. At the anode there was no bright spot, nor a trace of the second spectrum of hydrogen. There was a faint flickering striation, of the same colour and appearance as that in hydrochloric acid, too faint to shew a spectrum. The capillary gave the first spectrum of hydrogen without the second spectrum, but no oxygen lines.

That some decomposition of the vapour was produced by the discharge was shewn by a little increase of pressure, and the fact that after sparking for a few minutes a little permanent gas could always be pumped out of the tube.

Other gases which I have studied are the oxides of carbon. So far as I can see they each give, with a continuous discharge, but one spectrum in all parts of the tube, in the negative glow, the capillary, the striæ and the anode, it is the same spectrum for both carbonic oxide and carbon dioxide, and was faithfully described and figured by Ångström and Thalén, in their *Recherches sur les spectres des métalloïdes* before referred to, as the spectrum of carbonic oxide. It consists of a number of channelled bands degraded on the more refrangible side, and of a number of weaker bands, almost equally diffuse on their two sides, in the spaces between the degraded bands. These gases are very sensitive to the kathode rays, and give a bright negative glow, by which the course of the kathode rays may be readily traced. The light in all parts of the tube is nearly white, and in the striæ, which are easily produced, there is no perceptible difference of colour between the anode and

kathode sides of the striæ, as there is in the striæ of hydrogen and of nitrogen, nor such a well-marked position of the maximum of luminosity. There was no trace of the bands of the candle-flame spectrum in either of the two gases in any part of the tube, with such a discharge as I have used.

Another carbon compound examined was cyanogen. The observations were impeded by the rapid decomposition of the compound, and the blackening of the tube, but I was able to observe some effects of the discharge. When all carbonic acid gas had been completely removed, the tube refilled with cyanogen and the pressure reduced, on first passing the discharge striæ appeared fairly sharply defined and moving from the kathode rather quickly, but as decomposition proceeded the striæ became very diffuse and ceased to move. After pumping out and refilling and reducing the pressure to about 2 mm., the kathode glow was fairly bright and the dark space defined. The spectrum of the glow shewed a set of bright bands in the orange and yellow, which appeared, by their number, character and arrangement, to be the same as the bands in that region of the spectrum which are developed in the flame of cyanogen burning in oxygen, though I could not prove identity, not having such a flame at hand for comparison. Then there were besides two sets of bright bands in the blue and violet, which from their position and appearance I had no doubt were the cyanogen groups beginning at about λ 4600 and 4215 respectively. At the anode no blue or violet bands could be seen, only some continuous light in the orange and on to green, with traces of the bands in that region that were bright and well-defined in the kathode glow. At higher pressure the anode light gave these same bands distinctly, though not so bright as the kathode glow, while the blue and violet sets were still absent. At still higher pressure the blue and violet bands appeared at the anode as well as at the kathode. By this time the whole tube had become very black with the products of decomposition which could not be removed by pumping. The best observations were obviously those made at first, from which I gather that all the bands above mentioned belong to the kathode glow. In no case, when once the carbonic acid had been thoroughly removed, did I see anything of the spectrum either of carbonic oxide, or of the candle-flame, though the latter is always very brilliant in the flame of cyanogen fed with oxygen.

The series of bands less refrangible than the blue, so bright in the flame of cyanogen, are not connected with the series in the blue and violet. The latter are very bright, in both arc and spark, between carbon electrodes in nitrogen, without a trace of the former. The latter are degraded on the more refrangible side, while the former are degraded on the less refrangible side, which is such an important difference that I feel sure that the vibrating molecules in which they originate are different. This is probable enough because of the rapid decomposition of cyanogen in the discharge, and the

ease with which paracyanogen is produced, but at present I have no evidence for attributing the orange bands to any particular product of cyanogen.

Coming to the theoretical considerations which the facts observed suggest, we have to account for (1) the two perfectly distinct spectra, at the kathode and anode respectively, of hydrogen, nitrogen, and the halogens; (2) the absence of any anode light in oxygen and sulphur; (3) the identity of kathode and anode spectra in the metallic vapours, and in carbonic oxide; (4) the absence of visible spectra which can be ascribed to the compound molecules of hydrochloric acid and water, while the compound molecules of carbonic oxide and cyanogen give very characteristic spectra; (5) the identity of the spectra of the two oxides of carbon.

The appearances of the positive column in hydrogen and nitrogen agree well with Professor Thomson's theory* that the light of the column is excited by association of the ions, and arises in the positive ions. The head of the column nearly coincides with a region in which the strength of the electric field is a maximum, and this would occur where the association of ions is a maximum. Moreover, the spectrum of the head of the column, especially the brightest part of the head of each stria when striation occurs, is essentially that of the anode, and the head of the column is driven from the kathode as the exhaustion proceeds and the free path of the negative ions lengthened, until, when the dark space reaches to the anode, the second spectrum of hydrogen, and the closely set yellow bands of nitrogen, are seen only on the anode. These spectra are both extremely complicated, whence I infer that the molecules in which they originate are of complicated structure and comparatively massive. The continuous spectra of the halogens at the anode emphasises this point, they are, in a sense, still more complex, and it is noticeable that the brightness of the continuous spectrum is greatest in iodine and least in chlorine, in fact follows the molecular masses. In connexion with this it seems probable that oxygen may emit some continuous spectrum at the anode, feebler than that of chlorine, and not easily detected, because not lying in the part of the spectrum most easily seen.

The kathode glow follows so closely the course of the kathode rays, and the gases behave to them so precisely in the way that a fluorescent liquid behaves to ultra-violet light, that the inference immediately suggests itself that the excitement of luminescence is of the same sort in these two cases, and also in the case of the glass which fluoresces under the rays when the density of the gas is insufficient to absorb them.

The essential character of fluorescence, as I understand it, is that the fluorescing substance absorbs certain kinds of radiant energy and forthwith emits it again in a more or less modified form as light, and continues to do

* *Phil. Mag.* [5], 1, p. 278, 1900, and *Conduction of Electricity through Gases*, Cambridge University Press, 1903.

this as long as the exciting cause continues and for no appreciable time longer, and is not itself permanently changed in constitution or material by the process.

Percival Lewis' observations* have shewn that various metallic vapours exposed to kathode rays, without being in the course of the electric discharge, or forming part of the conducting gas, emit light, of which he has examined the spectra.

In the case of each of the four metals that I have examined, the rays that he found in its spectrum are all to be seen in the kathode glow of the same metal, though in sodium and cadmium the glow gives a greater number of rays than Lewis observed. But the most convincing argument that the molecules of the gas emitting the kathode glow are unaltered in constitution is that in many cases the spectra are reversible. This could not be unless the molecules which produce the reversed spectra by absorption, were the same as those which under the stimulus from the kathode emit the same rays bright. The line spectrum of hydrogen is well known to be reversed in the sun, and the reversal of *C* and *F* has often been observed in looking at a spark in dense hydrogen. Most of the metallic lines also which I have seen in the glow, as well as those Lewis has observed in the kathodo-luminescence of vapours of potassium, zinc, and magnesium, are reversible. But perhaps the most striking case is that of the cyanogen bands. The two sets of these bands which are conspicuous in the kathode glow in cyanogen are invariably associated with two other sets, ultra-violet, near the solar lines *L* and *N* respectively. Of these that near *L* is reversed when the flash of an arc is taken in an atmosphere of cyanogen, as Professor Dewar and I found†.

Wood and Moore‡ have recently obtained, as a fluorescence of sodium vapour in sun-light, a bright banded spectrum corresponding to the absorption spectrum of the same vapour described by Roscoe and Schuster§. I have little doubt that the kathode rays would produce a similar spectrum in sodium vapour of sufficient density, but could not try it because my glass tubes would give way at the temperature required to produce such dense vapour.

It is true that the oxygen lines and bands of the kathode glow have not been observed to be reversed, whereas some other absorption bands of oxygen are well known. I am not inclined to attach much weight to the former fact, and with regard to the latter it must be borne in mind that it requires a great thickness of compressed oxygen to make those absorptions visible, so that we could not expect to see the corresponding emissions from a small mass of gas at low pressure.

It is noteworthy that the persistent glow of radium salts in atmospheric

* *Astro-Phys. J.*, xvi, p. 31.

† *Astro-Phys. J.*, xviii, p. 94.

‡ *Supra*, p. 370, note.

§ *Proc. R. S.*, xxii, p. 362.

air is that of the kathode in nitrogen, as Sir W. and Lady Huggins have shewn*.

The behaviour of the metals suggests that the positive ions consist of molecules of the vapour, which when de-ionised vibrate to the same tune as do the like molecules under the influence of kathode rays. In this connexion the monatomic character of metallic vapours may have some significance. But be that as it may, the positive ions may very well be molecules of the vapour, and no reason occurs to me why chemically compound molecules, such as those of carbonic oxide, should not become positive ions. In fact these molecules often play the part of elementary atoms in chemical combination.

Of hydrochloric acid no emission spectrum has, so far as I am aware, been observed, and the only absorption spectrum it gives is a continuous one in the upper region of the ultra-violet, so that if it fluoresces at all the light it emits may be in that region. It is equally probable that the ions it furnishes may be derived from it by chemical dissociation. The absorption by water vapour is chiefly in the low red, and is only visible when the light has traversed a great thickness of vapour, while its emission spectrum is chiefly ultra-violet, so that it is *à priori* not improbable that it would give no visible fluorescence. It is also not improbable that the ions are furnished by dissociation of the elements, and the facts that water vapour gives no anode light, hydrochloric acid a continuous spectrum at the anode, lend confirmation to the supposition that oxygen furnishes the positive ions in the former, chlorine in the latter medium.

The identity of the spectra given by the two oxides of carbon suggests that the ions of carbonic acid gas are furnished by dissociation of carbonic oxide and oxygen. It is true that I have not been able to trace the presence of oxygen at the kathode as I was able to do in water vapour, but considering that in the latter case it was only blue lines of oxygen that were seen, and that they could not have been detected but for the fact that hydrogen gives no light in that region, it is not surprising if the very brilliant spectrum of carbonic oxide overpowered the oxygen.

It has been maintained that the common spectrum of the two oxides of carbon is emitted by carbon, but the fact that cyanogen, when all carbonic acid from the glass has been well pumped out, does not shew the carbonic oxide spectrum, is a strong reason for concluding that molecules of carbonic oxide are really the origin of the vibrations producing the spectrum in question.

In conclusion, the examination of the kathode glow, very incomplete as it is, has suggested to me that the explanation of the solar chromosphere and corona will be found in regarding them as a huge kathode glow.

* *Proc. R. S.*, lxxii, p. 409.

THE SEPARATION OF THE MOST VOLATILE GASES FROM AIR WITHOUT LIQUEFACTION

[*Proceedings of the Royal Society*, Vol. LXXIV. (1904), pp. 127 sqq.]

FROM the time when liquid air came to be an ordinary laboratory agent, I have continually used it for the purpose of producing high vacua in vessels that had been previously filled with easily condensable gases, like sulphurous acid, carbonic acid, vapour of water or benzol.

When the liquefaction of hydrogen was effected one of the first scientific uses to which it was put was that described in my paper on the "Application of Liquid Hydrogen to the Production of High Vacua, together with their Spectroscopic Examination*." In that communication it was shewn by theory and confirmed by experiment that the condensing power of liquid hydrogen is so great relatively to that of liquid oxygen or nitrogen, that any closed vessel, a part of which is cooled to the boiling point of hydrogen, must suddenly become a highly vacuous space. This was proved by the great difficulty of getting electric discharges to pass through specially prepared spectroscopic tubes when subjected to liquid hydrogen cooling, and from the fact that when the current did pass no lines of oxygen or nitrogen were seen, but only those of hydrogen, helium and neon. In order to separate these latter gases from air it was necessary to liquefy a quantity of air and to distil off the most volatile portion at as low a temperature as possible into a separate receiver placed in liquid hydrogen. In this way many spectroscopic tubes were filled with the uncondensable air gases and the results of their examination are recorded in a paper entitled "On the Spectra of the more Volatile Gases of Atmospheric Air, which are not Condensed at the Temperature of Liquid Hydrogen†," by Professor Liveing and myself.

Some two years later I improved the method of separation of the volatile air gases. The process is fully described and illustrated in my paper on "Problems of the Atmosphere‡." Its success depends upon the continuous

* *Roy. Soc. Proc.*, Vol. lxiv, 1898.

† *Supra*, p. 484.

‡ *Supra*, p. 506.

direct liquefaction of air at atmospheric pressure combined with a device which enables the more volatile gases to be trapped and separated. In this way some 1/35,000th of the volume of the air liquefied is collected as a gaseous mixture, having the composition 38 per cent. of nitrogen, 4 per cent. of hydrogen, and 58 per cent. of mixed helium and neon. After sparking to remove the nitrogen and hydrogen, a gaseous mixture of helium and neon containing a little argon was obtained. This mixture had the composition of 16 per cent. helium and 84 per cent. neon. In both methods of treatment it will be noted the liquefaction of the air was the essential preliminary operation, to be supplemented in the one case by the use of liquid hydrogen, in the other by sparking to remove the nitrogen. The paper already communicated to the Royal Society*, entitled "The Absorption and Thermal Evolution of Gases Occluded in Charcoal at Low Temperatures," in which the greatly increased power of occlusion possessed by charcoal at low temperatures is proved, suggested an inquiry into the limits of gaseous pressure reached by such means of condensation.

With this object a narrow tube CE, fig. 1, was sealed to an ordinary spectroscopic sparking tube AB, and at the end E an enlarged space was blown out capable of holding a few grammes of cocoanut charcoal. After the charcoal had been freed from gases by heating and exhaustion and the poles cleared by sparking during this operation, pure and dry gases like oxygen, nitrogen, air, carbonic oxide, hydrogen, neon and helium could be admitted at different pressures and the tube with its charcoal chamber attached sealed off.

On placing the charcoal end of the apparatus in liquid air the gas in each case was rapidly absorbed and the vacuum produced reached the phosphorescent stage in all cases with the exception of hydrogen, neon and helium. A small Crookes's radiometer, full of air at atmospheric pressure, with charcoal tube attached, became quite active to heat radiation when the charcoal was cooled for half a minute in liquid air. To test the amount of exhaustion reached by the use of a given weight of cocoanut charcoal I sealed on a tube containing 30 grammes to a large electric discharge tube of 1300 c.c. capacity filled with air at atmospheric pressure. On cooling the charcoal receptacle in liquid air the pressure diminished to 50 mm. of mercury. Repeating the same experiment but starting with the tube initially at half an atmosphere, the exhaustion reached was now beyond the striæ stage. A further experiment starting with one-fourth of an atmosphere gave a vacuum through which no discharge passed.

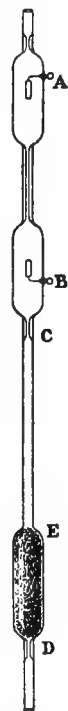


FIG. 1.

* *Roy. Soc. Proc.*, Vol. lxxiv, p. 122.

Finally, the 30 grammes of charcoal were replaced by only 1 gramme and the initial pressure was reduced to 3 mm. of mercury. Now the vacuum just reached the beginning of the phosphorescent stage. With hydrogen, either a pressure of gas less than that of the atmosphere had to be used at starting or a larger amount of charcoal employed in order to get a vacuum well up in the striæ stage. If, however, the liquid air was cooled to -210°C . by exhaustion, the tube just reached the beginning of phosphorescence round the cathodes.

With helium there was a very slight absorption, but neon did shew something more appreciably. Spectroscopic observations made during the condensation of the gas in the charcoal shewed the gradual disappearance of the characteristic spectrum of oxygen, nitrogen and air, as the high vacuum was reached and the discharge passed with great difficulty. In tubes of this kind filled at atmospheric pressure I could always see the F line of hydrogen and the neon yellow; but the helium was not seen with any definiteness. As the amount of neon in the air cannot well exceed 1/50,000th, the spectroscopic test is very delicate.

In order to bring in the helium lines it was necessary to concentrate the volume of air in the space of the sparking tube six or seven times. This was done by the use of an arrangement shewn in fig. 2. AB is the sparking

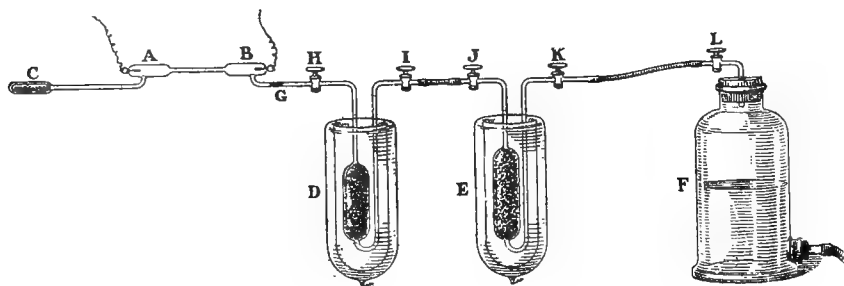


FIG. 2.

tube with its small charcoal bulb C attached, capable of being sealed off when required at G; and D and E are larger charcoal absorbers placed in vacuum tubes containing liquid air; the whole being attached to a graduated gas-holder F containing air. A series of glass stop-cocks are attached at the points H, I, J and K in order to facilitate manipulation. In determining the volume of air required to bring in the helium lines only one charcoal absorber containing about 15 grammes of material was used. On allowing 200 c.c. of air from the gas-holder to be sucked into the charcoal (which had been previously exhausted along with the sparking tube), on opening the stop-cock H any residuary gas in D was swept into the sparking tube, which was then sealed off at G.

This tube gave the hydrogen lines C and F, the neon yellow, and some of the orange lines, along with the helium yellow and green quite distinct. With the residuary gas extracted from 1 litre of air I could see all the helium lines. On the positive pole the neon yellow and the green of helium were alone marked, while the negative pole gave both the neon and helium yellow lines along with the helium green and the F of hydrogen on the continuous spectrum. From this it would appear that the spectroscopic test for helium is as delicate as that for neon, and that 1/50,000th can be recognised. From 3 litres of air discharge tubes were obtained giving the neon and helium spectra associated with a brilliant ruddy glow discharge.

As 40—50 grammes of charcoal can absorb at the temperature of liquid air from 5—6 litres, it is easy to accumulate rapidly the uncondensed gases in considerable quantities for spectroscopic examination. For this purpose I found it convenient to use two charcoal condensers in circuit as represented in fig. 2. After the charcoal in the first one marked E was saturated, the stop-cock K was closed, while I and J were opened for a short time so as to allow the less condensable gas in E to be sucked into the second vessel, of the same type D, along with some portion of air. The charcoal condenser E was then taken out of the liquid air, and rapidly heated to 15° C. in order to expel the occluded air. It was thus in a condition to repeat the absorption. In this way 50 litres of air can be treated in a short time. Sparking tubes filled from the accumulated gases in D were very brilliant, shewing the complete spectrum of the more volatile constituents of air. It is hardly necessary to remark that after the little charcoal receptacle connected to each of the sparking tubes has been cooled and thus all traces of air absorbed, it can be sealed off, leaving the spectroscopic tubes intact. The complete spectroscopic study of the products must be left for further examination with Professor Liveing.

The method I have described will be equally applicable to the treatment of the gaseous products from minerals containing helium, hydrogen, etc., and also to the radium products of a similar kind. It seems even probable that the separation of the less volatile constituents in air may be improved by a slight modification in the mode of working. The behaviour of the gases from the Bath Springs has been examined. When the gas containing 1/1000th part of helium in what may be regarded as pure nitrogen is subjected to charcoal absorption, exactly in the same way as the air was treated, no high vacuum is reached. All the nitrogen and any other constituents disappear, and a spectrum of helium and hydrogen shewing much less neon than exists in the volatile residue from atmospheric air is the result. A sample of argon made from Bath gas gave, when the argon was absorbed in charcoal, a gas residuum giving the helium and neon spectrum, and the same result follows the use of atmospheric argon. In the case, however, of the Bath gas

argon the helium spectrum is the stronger, whereas with air argon the neon is the most pronounced.

In order to further test the method, the crude gases got by heating the mineral Fergusonite were examined. During the cooling of the charcoal the nitrogen and hydrogen spectra were marked, but in a short time nothing could be seen but the lines of hydrogen and helium.

Great interest will attach to the behaviour of helium, hydrogen and the most volatile part of air, when subjected to the action of charcoal cooled to the temperature of liquid hydrogen. The method promises to open up many avenues for future inquiry.

Supplementary memoir, not heretofore published, on the separation of gases, and the spectroscopic detection of certain gases which form small percentages of gaseous mixtures

ON THE SEPARATION OF GASES BY ELECTRIC DISCHARGES WITH VARIOUS ELECTRODES

Action of copper oxide on the gases evolved from uraninite on heating

THE apparatus is indicated in fig. 1: CD is a long glass tube returning upon itself, but having an ordinary sparking tube in its course, and a branch with a small bulb, A, at its end. In this bulb was placed the mineral which evolved gas when heated. One electrode of the sparking tube was a copper wire on the end of which a small globule had been melted, and superficially oxidised, by an oxy-hydrogen blowpipe. The other electrode was of aluminium. One bend, D, of the long tube could be cooled by dipping it in a vessel of liquid air, and be allowed to rise in temperature again by lifting it out of the liquid air.

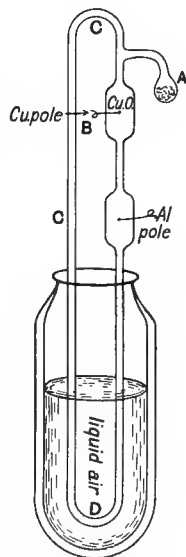


FIG. 1.

In the first experiment the mineral in A was Ceylon uraninite which had been previously heated and the gas exhausted. The whole apparatus was exhausted very completely and sealed up in the exhausted state. The bulb with the mineral was then heated slightly so as to produce a small pressure of gas in the tube. After cooling the bend of the tube in liquid air, the spark in this gas shewed the spectra of hydrogen and carbon monoxide. After a second heating of the mineral the spectra were those of helium and hydrogen. After continued sparking the hydrogen entirely disappeared and the spectrum of helium only remained. On again heating the mineral, hydrogen and helium were again given off, and after sparking the hydrogen again disappeared. This was repeated many times, always with the same result, except that the pressure of the residual helium diminished under continued sparking until its spectrum, as well as that of

hydrogen, finally disappeared. The pressure in the tube was estimated by the length of air-gap, in an external parallel circuit, which the spark would overleap without visible discharge through the tube.

Whenever, after heating the mineral, there was no continued sparking the spectra remained unaltered for an indefinite time, and so it was if the sparking were continued for a time not long enough to efface the hydrogen. Therefore the mineral did not re-absorb any of the gases. No doubt the hydrogen and any hydrocarbon, as well as carbon monoxide, would all be oxidised by the copper oxide of the electrode, and the products be condensed in the cooled part of the tube. The helium must have been absorbed by the electrodes or by the material thrown off them in sparking. This explanation is confirmed by other observations. When the current had been going in one direction for a time, so that the spectrum of hydrogen was much weakened, on reversing the direction of the current, the spectrum came out stronger, indicating that some of the hydrogen had escaped oxidation and been absorbed by the aluminium electrode. Also after long sparking, when the greater part of the oxide had been spurted off the copper electrode, the removal of the hydrogen became very slow, and finally ceased.

The current passed easily when the aluminium pole was the negative one, but with difficulty in the opposite direction. And on heating the deposit about the copper oxide electrode, without heating the aluminium electrode, some gas was evolved, the hydrogen lines became more marked and the helium brighter, and the difference of the resistance on reversing the current disappeared. The electrodes were polarised, as in electrolysis, by occluded gases.

Another experiment was made with a re-entering tube similar to that shewn in fig. 1, except that both electrodes were of aluminium and there was no branch tube. This tube was filled with dry hydrogen at about 10 mm. pressure, and the lower bend cooled as before in liquid air. After two hours' sparking the resistance to the passage of the spark through the tube became very high, and, without condenser, the spectrum shewed the lines C and F of hydrogen, bands of carbon monoxide, and continuous light (fluorescent). With condenser in circuit, it shewed in addition bands of nitrogen and some lines of the second spectrum of hydrogen. On lifting the tube out of the liquid air, the resistance diminished, and the spark behaved as in an ordinary tube with a residue of hydrogen at 2 or 3 mm. pressure, and gave the second spectrum of hydrogen strong, with and without a condenser. A sponge of liquid air applied to it gave rise to a visible deposit. After replacing the bend of the tube in liquid air, and half an hour's sparking, the second spectrum of hydrogen had diminished and soon after disappeared*, the

* This is what occurs usually with hydrogen, when the exhaustion is carried so far that the negative stream passes right through the capillary; the second spectrum of hydrogen is then seen only on the sheath about the positive electrode.

resistance having become very high. On taking the tube out of liquid air again, the resistance fell and a fine spectrum of hydrogen reappeared. As it was again cooled the spectrum passed through a stage in which the spark, without a condenser, gave the nitrogen bands, and with condenser the brightest rays of the line spectrum of nitrogen. On repeating these experiments the same changes occurred again. It would appear that the glass must have retained some air and carbon dioxide, which would supply some oxygen to form water with some of the hydrogen: but there could hardly be oxygen enough from this source to produce so much water as to give a visible film on the cooled spot of the tube, nor would it have required two hours' sparking to bring about the reduction of pressure when the water vapour was condensed in the cool part of the tube almost as fast as it was formed. It looks as if oxygen were obtained by some decomposition of the glass by the sparking.

What very unexpected results may be obtained from the decomposition of the glass of sparking tubes appears from the following experiments. Three samples of gas were observed, and a Leyden jar was in circuit.

I was gas expelled by heat from charcoal from which the more volatile gases had been extracted in the cold. A sparking tube, to which a bulb with charcoal was attached, was filled with this gas and then the charcoal bulb cooled in liquid air.

II was the residue of the most volatile part of air after it had been passed through a tube containing charcoal cooled to 60° abs.

III was helium from the Bath spring after it had passed through a tube with charcoal cooled in solid hydrogen at 15° abs.

The wave-lengths of lines observed in the spectra of these gases are tabulated below along with their probable origin:

I λ	II λ	III λ	Probable element	
5220	5220	5217	Cl	5221·5
5320			S	5320·8
5346			S	5345·8
5393	5395	5394	Cl	5392·3
	5403		N bd	5401·8
5422	5424	5424	Cl	5423·4
5431			S	5428·9 and 5433
5444	5445		Cl	5443·6
		5450	CO	5449

The only credible explanation of the appearance of the rays common to all three tubes is that the gases producing them were derived from the tubes themselves by the action of the electric discharge. The glass may probably

have traces of chlorides and sulphates in its composition which were decomposed by the spark.

A subsequent experiment was made with a tube with platinum electrodes. The tube was a re-entering one like the last, except that it had a lateral bend which was wrapped in cotton wool in a vacuum vessel (fig. 2), and cooled from time to time by wetting the wool with liquid air*. It was filled with hydrogen at 10 mm. pressure to begin with. This was sparked for an hour without any sign of increased resistance to the passage of the spark. Suddenly the resistance increased so that the spark gap in the parallel circuit had to be increased from $\frac{1}{4}$ inch to $1\frac{1}{2}$ inch to prevent the discharge passing that way. On allowing the cooled bend to warm up, the resistance fell, until it was less than that of the by-circuit with a $\frac{1}{4}$ inch gap. Merely cooling the bend again did not raise the resistance and some minutes' sparking hardly changed it; but after sparking about 15 minutes the gap in the by-circuit had to be increased to $1\frac{3}{4}$ inch to prevent the discharge passing that way, and even then the luminous discharge passed through the longer wide part of the tube and not through the capillary. Several repetitions of this treatment resulted in the same effects, but after these it was found that merely cooling the bend without sparking increased the resistance, and finally a high resistance was produced by cooling alone, so that no readily decomposable compound had been formed by sparking. Well marked lines of the second spectrum of hydrogen were observed when the tube was allowed to warm up. In this tube the glass around the platinum wires was found to be partly fused in black globules; so that there is not much doubt that the hydrogen had been gradually oxidised at the expense of the material of the glass.

Another tube with platinum electrodes, treated as before, failed to give high resistance.

Next, two similar tubes, one with aluminium electrodes and the other with oxidised copper electrodes, were put up in communication with each other by a tube which could afterwards be sealed by fusion. During the sparking much fine metallic copper was deposited on the glass about the oxidised copper electrodes, and it was afterwards found that all the oxide had

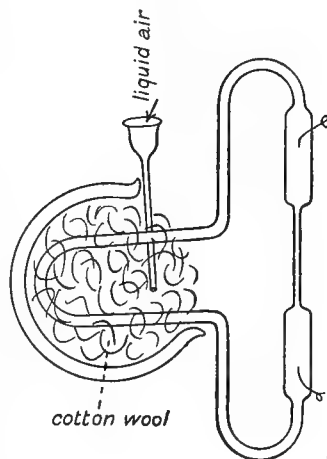


FIG. 2.

* It will be noted that in a tube of the form of fig. 1 there is no tendency of the gas to circulate by convection, inasmuch as the cold bend is at the bottom, and the cold gas being the most dense will stay there; whereas in the tube with the lateral cooled bend of fig. 2 there will be a flow of cold dense gas to the lower bend where it will be warmed again and so circulate.

been reduced to metallic copper. After sparking, and condensation of the water formed in the cooled bend of this tube with copper electrodes, it was sealed off, and the sparking of the tube with aluminium electrodes continued. The resistance increased and the residual gas gave only the line spectrum of hydrogen.

Another experiment with a tube of the form of fig. 1, with electrodes of iron coated with black oxide, gave similar results. The iron oxide seemed to clear out the spectra of carbon oxide and hydrogen better than the copper oxide. To remove the helium took a longer time of sparking, and when the exhaustion had become so great that the tube became phosphorescent, the green helium line could still be seen, and on heating the deposit on the glass the resistance fell and the spectra of helium and hydrogen reappeared.

In a tube with electrodes of oxidised nickel and one centigram of mineral no hydrogen got through the cold bend, but on letting the bend heat up both carbon oxide and hydrogen made their appearance. This seems to shew that all the hydrogen given out was in the form of water. The tube was then put away for three days to see whether any helium came out at the ordinary temperature of the air. It was found then that when the bend was cooled the resistance was very high, and forcing the discharge brought out only the sodium line and no helium. When the mineral was once more heated helium substantially pure came off without hydrogen or carbon oxide. This helium was absorbed on sparking. The mineral was then further heated up to the fusing point of the glass, but still no hydrogen and only a trace of carbon oxide appeared.

The helium was absorbed by the copper, or the copper oxide, deposited on the glass, and was evolved again on heating the tube at that part. Another tube, with two metallic electrodes, containing helium at low pressure, shewed increased resistance on sparking, but the helium was not easily absorbed, and finally the spectrum consisted of the yellow and green lines only, $\lambda 5875.8$ and $\lambda 5015.7$.

This tube shewed no radio-activity when left on a photographic plate for 24 hours.

One gram of the Pollusk meteorite, treated in the same way as the Ceylon mineral had been treated, but in a tube like fig. 6 (p. 547), gave the spectra of hydrogen and carbon oxide just as marsh gas does: the copper oxide completely oxidised it after a time and the resistance became very high. No helium line, or nitrogen, shewed, and on taking the bend out of liquid air the pressure inside the tube became high, and much water was apparent.

Cleveite, similarly treated, gave the spectra of hydrogen and nitrogen; and at the poles that of helium. The amount of nitrogen was so great that, on sparking, the copper oxide poles did not easily remove it. After some

hours' sparking the yellow and green helium lines could be seen in the capillary superposed on the nitrogen bands. Subsequent heating and sparking always gave more nitrogen, but no more hydrogen and no carbon oxide spectrum. The nitrogen in each case was absorbed after continued sparking and a pure helium spectrum left.

The tube, with the bend attached, was next opened and sealed on to the air pump, and exhausted. On heating the deposit about the electrodes the carbon oxide spectrum was strong, and when this had been removed by cooling the bend, nitrogen appeared and after its absorption the spectrum was that of pure helium. When the bend was taken out of the liquid air the nitrogen spectrum reappeared, so that some had been oxidised and condensed. When the sparking was continued while the bend remained at the ordinary temperature of the air the nitrogen spectrum disappeared again.

Gases from Borrowdale graphite.

Borrowdale graphite was heated in a tube of the form represented in fig. 3, so that the gases evolved passed through the cooled bend before reaching the sparking tube. Both electrodes were of oxidised copper. The spectra seen were those of carbon oxide and hydrogen, and after some sparking the copper oxide electrodes took out these gases entirely, but time was necessary. Analysis of the gases evolved by a specimen of the graphite, which had a specific gravity 2.86 and evolved on heating 2.6 times its volume of gas, shewed them to consist of CO_2 , 36.4; CO , 7.77; H , 22.2; CH_4 , 26.11; N , 6.6. It appears therefore that carbon monoxide, or a mixture of hydrogen and marsh gas, is not entirely condensed at the temperature of liquid air, but that all the gases are oxidised by the copper oxide with continued sparking.

When a mixture of zinc acetate and lime replaced graphite in this experiment, the spectrum of the gas evolved was the same as for graphite, and sparking took all out as before.

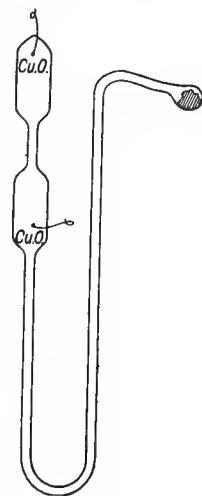


FIG. 3.

When 0.05 grm. of Borrowdale graphite was heated with copper oxide and the gas evolved passed through the bend immersed in liquid air, that which escaped condensation gave the spectra of hydrogen and carbon oxide, and the former disappeared with continued sparking. On taking the tube out of the liquid air the spectrum was still only that of carbon oxide, but the pressure much higher. With a jar in circuit the hydrogen lines came out and little else.

Action of other electrodes.

A tube of the form shewn in fig. 4 had liquid alloy of sodium and potassium completely covering the platinum electrodes at the two ends of the tube, and contained atmospheric air. It was exhausted until the pressure was reduced to 5 mm., and on sparking shewed the banded spectrum of nitrogen and the green line of mercury; but suddenly the nitrogen disappeared and only a faint spectrum of argon remained visible. A tube containing charcoal which could be cooled in liquid air was now attached, and the whole filled up with atmospheric air at normal pressure. By cooling the tube containing charcoal no high vacuum could be obtained. The spectrum was the first and second spectra of hydrogen along with the yellow line of neon, and, when a jar was in circuit, the sodium line also. After continued sparking for half an hour, or more, there was no apparent

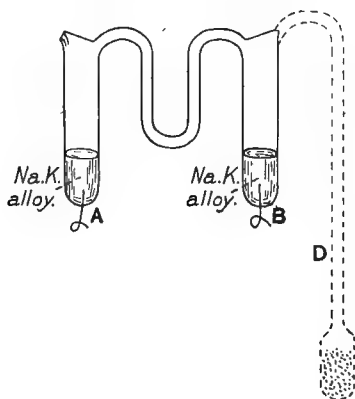


FIG. 4.

absorption of hydrogen. The temperature of the charcoal was allowed to rise while the sparking was continued, and then was again cooled, and this oscillation of the temperature repeated two or three times. The resistance was now higher, the hydrogen gone, and only the yellow line of neon and remnants of the glow bands of nitrogen visible. On cooling the charcoal slowly the spectrum of argon could be seen at an intermediate stage of the exhaustion. The blue set of argon lines were visible as well as the red, the lines $\lambda 6172$ and $\lambda 6415$ being most persistent. An attempt to get the nitrogen absorbed by the sodium and potassium on continued sparking while the temperature of the charcoal oscillated, was unsuccessful. The tube was left standing all night and was found unchanged next day: still shewing no hydrogen; but argon lines when a short length of the charcoal is carefully cooled, and the nitrogen bands fade in the yellow and red, and the negative glow of nitrogen, about $\lambda 4709$, is left. This charcoal had been made from the wood used for making bobbins and was very light but very active. The

tube containing it was next replaced by one with cocoanut shell charcoal, which, however, behaved in exactly the same way.

Tubes with aluminium electrodes containing atmospheric air and different varieties of charcoal were examined, and all gave the spectrum of hydrogen, which did not disappear on sparking with alternate warming and cooling, nor did the argon spectrum come out in them as it did in the tube with the sodium alloy. The argon lines read had wave-lengths 7504, 7384, 7067, 6938, 6415, 6170?, 6052. The tubes were opened and some sodium-potassium alloy placed on one of the aluminium electrodes in each tube. After sealing them up again and cooling the charcoal, but not so as to produce a very high resistance, the spark shewed only the first and second spectra of hydrogen. When the sparking was continued, and the pressure allowed to rise, the hydrogen disappeared; and after allowing the nitrogen spectrum to develop and then cooling the charcoal slowly, the argon lines came out.

When a tube of the form shewn in fig. 4, but with one electrode (B) aluminium and the other (A) sodium-potassium, was used, the resistance was much greater when the aluminium was the negative pole than when the current passed in the opposite direction. In the latter case the current passed easily and a fine phosphorescent glow extended down the side tube D to the charcoal, and shewed the negative glow bands of nitrogen. There was no glow when the direction of the current was reversed. The tube was opened and air admitted, which was exhausted to 10 mm. pressure and the tube then sealed up. On sparking, the spectrum of hydrogen was seen for a time only, and then observing carefully as the cooling of the charcoal proceeded, the argon lines were seen, especially in the green, and along with them the neon line very faint. Neon had not been noticed before when the pressure of the air in the charcoal tube at starting had been less than 6 inches.

In another tube metallic calcium instead of sodium-potassium was put round one aluminium electrode. After cooling, only a strong spectrum of hydrogen appeared, no nitrogen, even when the pressure of the residual gas was allowed to rise. After a fresh admission of air, which was then exhausted to a pressure of 10 mm., the calcium failed to absorb the nitrogen.

On repeating the experiment with a tube having both electrodes of sodium-potassium, starting with air at 5 to 10 mm. pressure, the spectra of hydrogen and nitrogen soon disappeared and then the argon spectrum was seen.

This tube was opened and exhausted and refilled with an old krypton residue to a pressure of about 10 mm. After sparking, all the nitrogen disappeared and a fine krypton spectrum was left. If the tube were allowed to stand for an hour or more, nitrogen came out of the charcoal but was easily absorbed again on sparking. Readings were taken with a one-prism

spectroscope, and reduced to wave-lengths. These wave-lengths are here tabulated, along with the probable origin of each ray:

λ	Probable origin	λ	Probable origin
7581	Kr 7601	5506	N bd 5510
7053	Ar 7067	5495	{N bd 5495
6950	Ar 6965		{Ar 5496
6455	O 6455	5472	{N bd 5473
6417	Ar 6416		{Xe 5473
6238	N bd 6243	5227	N bd 5227
6140	Ar 6146	4970	O 4968
6071	Xe 6068	4766	Kr 4766
6040	{Ar 6043	4738	Kr 4739
	{Xe 6036	4488	Kr 4490
6003	N bd 6006	4455	Kr 4454
5995	N bd 5990	4444	Xe 4448
5872	Kr 5871	4364	Kr 4363
5842	N bd 5847	4308	emanation?
5634	Kr 5633	4259	Ar 4259
5557	{Kr 5562		
	{Ar 5559		

On cooling the charcoal with liquid air all the krypton was absorbed and argon lines left. At the limit the neon lines shewed and traces of the blue argon spectrum. On cooling the charcoal with solid carbon dioxide, the greater part of the krypton was condensed and the argon came out. The full pressure of the krypton in the tube was not more than 5 mm.

A sample of gas from the last portion evaporating from liquid air was condensed by passing through a U-tube, containing charcoal, cooled to -110°C . (solid alcohol) and was allowed to evaporate at a temperature below -80°C ., by placing the U-tube in solid carbon dioxide. The U-tube was then sealed on to a sparking tube with sodium-potassium electrodes which was connected by sealing to a mercury pump, and the discharge examined with a spectroscope as the exhaustion proceeded.

At first nothing was seen but nitrogen, but after a time the krypton green lines were easily seen on a background of nitrogen. On shutting off the gas supply and sparking, the argon lines were strong.

Old charcoal which had had liquid air evaporated from it and had been left for months in the open flask did not give any krypton when examined as above, but only argon. Even on heating it, when carbon dioxide came off in plenty, the spark shewed only argon.

Studies of the dissociation of water vapour and of carbon dioxide, by electric discharges in vacuum tubes without internal electrodes, at pressures from 10 to 20 mm., and cooling with liquid air.

The tubes had a capillary, and external electrodes of tinfoil. One end was cooled, from time to time, by dipping in a vessel of liquid air, as shewn in fig. 5.

The water in one of these tubes was boiled, frozen, and exhausted. At the ordinary temperature of the air the electric discharge through it shewed the F line of hydrogen and C very faint, and the green bands of oxygen. After cooling one end in liquid air, the resistance became very high and the spectrum was reduced to F and a continuous spectrum. After taking the tube out of the liquid air and letting it warm up, the spectrum was that of carbon monoxide with all the lines of hydrogen, and the second spectrum of hydrogen also. As the sparking continued the CO bands disappeared, and finally the spectrum consisted of F only with a continuous background (phosphorescent).

A second tube similarly treated gave the same results.

Another tube was filled with carbon dioxide from fused sodium carbonate and boric oxide contained in a tube, which had previously been repeatedly heated and exhausted.

On starting the electric discharge, at the ordinary temperature of the air, the spectrum consisted of the five bands of carbon oxide and nothing else.

On cooling one end in liquid air these bands quickly disappeared, and the C line as well as the second spectrum of hydrogen appeared. Readings were taken of a number of the lines, and they were all found to correspond to lines of the first or second spectrum of hydrogen. After long sparking, with one end of the tube in liquid air, there remained plenty of gas in the tube to make the discharge visible.

It was noticed when the cooled end of the tube was made the negative electrode, the resistance was higher than when the cold end was positive.

The permanence of the hydrogen spectrum (so-called) suggests that it may be due to some uncondensable hydrocarbon.

A fresh tube, first thoroughly cleaned and ignited in air at a red heat, was filled with carbon dioxide from the same mixture as before, but the gas was first condensed in a small U-tube containing phosphoric anhydride cooled in liquid air, from which the gas evaporated into the sparking tube when the temperature of the U-tube was allowed to rise. On passing the discharge through this tube with one end in liquid air, the resistance was found to be

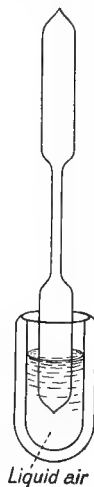


FIG. 5.

very high, and the spectrum only a green band on a continuous background from the phosphorescent glass, without a trace of hydrogen.

Sparked again at the ordinary temperature of the air for some time and then cooled, the result remained the same, and was still the same, after repeating that process.

Two new tubes were filled with the vapour of water which had been prepared from a mixture of caustic potash and potassium chlorate partly fused, condensed in a U-tube immersed in liquid air, highly exhausted, allowed to evaporate, and again exhausted, several times. One of the tubes had in it a fragment of fused caustic potash. On sparking at 15°C . the tube with no potash gave the bands of carbon oxide and the lines of hydrogen, and, on cooling, only the first and second spectra of hydrogen. On allowing the temperature to rise again only the carbon oxide shewed for a time, but finally nothing but the F line of hydrogen was well seen. Subsequently, on cooling and sparking, the resistance in the tube became very high, the carbon oxide shewing at first, and the first spectrum of hydrogen continuing until at last no lines, only a continuous spectrum, was visible. The second spectrum of hydrogen was not seen at any time.

The tube containing potash never shewed any carbon oxide bands. At starting it gave only the first spectrum of hydrogen and some lines of the second, and, after cooling, the latter became less marked, but the resistance never became very high. The residual gas must have been hydrogen, and the dissociated oxygen absorbed, perhaps by the potash with formation of peroxide, or a percarbonate.

A tube filled with carbon monoxide, made by passing the vapour from nickel carbonyl mixed with phosphoric anhydride through a hot tube and then through a tube cooled in liquid air, shewed, on sparking at 15°C ., a pure spectrum of carbon oxide. On cooling one end of the tube the resistance rose very rapidly, and at the limit of the exhaustion no spectrum but that of carbon oxide could be seen; no hydrogen line was visible. The conducting residue of gas must have been carbon monoxide.

Tubes filled with oxygen, prepared from potassium permanganate, to a pressure of 10 mm., shewed at 15°C . the bands of carbon oxide, but after cooling and sparking they disappeared and the green bands and the red line of oxygen formed the final spectrum.

Another tube, filled with oxygen from permanganate to 5 mm. pressure, contained carbon dioxide, which rapidly disappeared on cooling and sparking, leaving a very clean oxygen spectrum. The resistance in this tube never became very high.

Quantitative experiments on the spectrum of helium at measured low pressures.

An experiment was made with a tube of the form of fig. 1 with poles of oxidised copper, to determine whether the helium from 5 milligrams of uraninite could be detected. The total volume of the tube was about 18 cubic centimetres, and the volume of helium which can be got out of that mass of mineral is, at atmospheric pressure, about 20 cubic millimetres or $\frac{1}{900}$ th of the volume of the tube. After exhausting the tube and heating the mineral, the resistance in the tube was still very high and the discharge made the tube phosphoresce, but the yellow and green lines of helium were visible on the continuous background. With a much narrower tube of the form of fig. 2, so that the gas coming off the mineral passed through a cooled bend before reaching the sparking tube, the helium spectrum came out strong and all carbon oxide and hydrogen were removed by sparking. On taking the bend out of the liquid air, the carbon oxide bands came out strong and no helium was seen, then after a little time the helium spectrum was seen faintly, then the hydrogen, and finally, when the tube attained the temperature of the air, the hydrogen spectrum only; except at the negative pole where the yellow ray of helium still shewed.

This experiment was repeated with a tube of the form shewn in fig. 6,

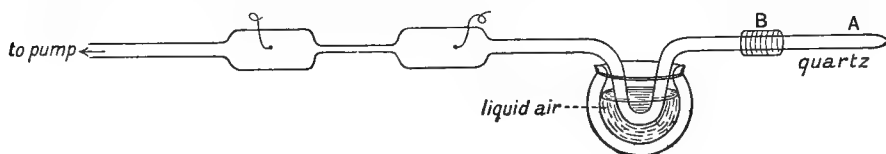


FIG. 6.

which had a quartz tube A, closed at one end and cemented at B to the glass tube. The glass tube had a bend which dipped into liquid air between B and the sparking tube and beyond the sparking tube was prolonged and connected with the air pump. The electrodes were aluminium.

The mass of Ceylon uraninite put into A was one milligram, and was heated with a blowpipe flame. The exhaustion of the gas in the tube remained very high, but there was enough to conduct the discharge, producing a bright green phosphorescence about the negative pole. In the capillary the F line of hydrogen was distinctly seen accompanied by two green bands, which the reading of the spectroscope shewed to be due to oxygen, and the green line, $\lambda 5015$, of helium. The same helium (*par*-helium) line was brighter in the wide part of the tube about the positive pole. The yellow helium line was not seen. During this examination the resistance increased, and on heating the glass about the electrodes with a spirit lamp, the first and second spectra of hydrogen were strongly developed.

In an experiment with apparatus like that shewn in fig. 6 a bulb of about 100 c.c. capacity as well as a U-tube were inserted between the quartz and sparking tubes. The volume of the bulb and U-tube together would be about 120 c.c., and 5 milligrams of the Ceylon mineral were placed in the quartz tube, which would give helium enough to fill, at the atmospheric pressure, about $\frac{1}{80000}$ th part of that volume. After exhausting the whole apparatus and then filling with helium by heating the quartz end, the resistance was still so high that the glass was phosphorescent, but the discharge passed freely. All the helium lines except the red one, $\lambda 6678$, were seen in the spectrum. When the bulb was sealed off, and patches of tinfoil attached outside it, the discharge passed through it easily and shewed chiefly the green ray of helium.

In the next experiment a vacuum tube without sealed in electrodes was employed. The tube was of shape shewn in fig. 7. The wide parts were

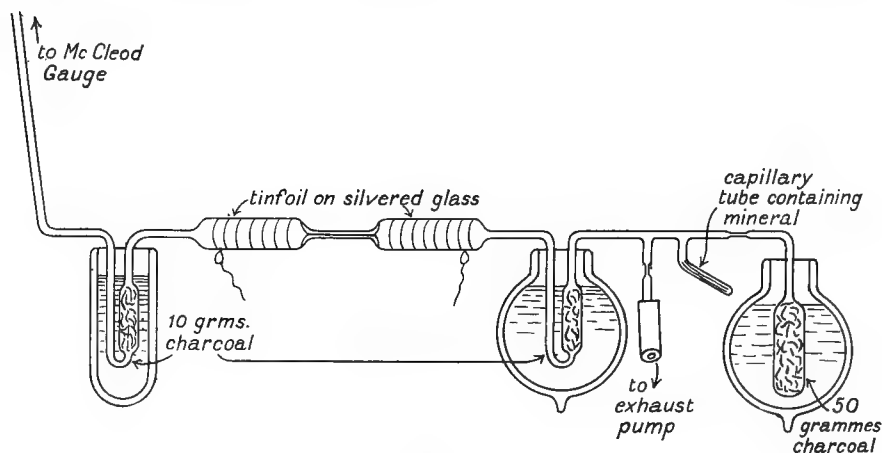


FIG. 7.

silvered on the outside, and contact was made by tinfoil bound on with copper wire. Two bulbs with charcoal, each containing 10 grams, were sealed on, one at each end of the sparking tube. The McCleod gauge was sealed on at one end of this arrangement, while to the other was attached the large charcoal bulb for final evacuation of the apparatus. A side tube for attachment to the exhaust pump (afterwards sealed off), and a quartz tube containing rather less than 0.5 gram. of uraninite, which when heated gave off the required helium, were also attached, a Faraday wax seal being employed for the quartz tube. Of the two 10 gm. charcoal bulbs, the one serves when cooled to keep the vacuum tube free from mercury vapour from the gauge, while the other absorbs gases other than helium, coming from the heated mineral. This bulb proved sufficient to ensure that only helium was present

in the vacuum tube; the traces of hydrogen which were evolved were all absorbed in this bulb at liquid air temperature.

After the whole apparatus had been exhausted down to less than 1 cm. pressure by the exhaust pump while the charcoals were heated, the exhaust connexion was sealed up, and the whole apparatus evacuated to a low pressure by cooling the large charcoal bulb in liquid air. When the pressure had been reduced to 0.006 mm., the two 10 gm. charcoal bulbs being heated during the exhaustion, the large charcoal bulb was sealed off, and the two 10 gm. charcoal bulbs cooled in liquid air. The quartz tube containing the mineral was then heated to redness with a Mecker bunsen burner. Electric discharge was at once easily obtained through the tube, and the pressure measured on the McCleod gauge found to be 0.1931 mm. This pressure remained the same after two hours. A pure helium spectrum was thus obtained. The discharge had a purplish green colour. The spark gap in the parallel circuit was 12 mm. There was slight phosphorescence of the glass round the negative pole. The hydrogen lines C and F were looked for, but were not present, the only lines seen being those of helium.

The two 10 gm. charcoal bulbs were now allowed to warm up: the pressure rose to 0.3821 mm. The hydrogen C and F lines were easily visible along with the helium lines. The spark gap had, however, to be slightly increased. The discharge had a pale lilac colour.

In the next experiment the quartz tube was replaced by a piece of barometer tubing of 2 mm. bore to contain about the same weight (0.5 gm.) of uraninite. Proceeding as before after exhausting, the helium was expelled in small quantities by gentle and progressive heating of the mineral by a spirit lamp. The preliminary exhaustion of the apparatus was carried to 0.0013 mm. before heating the mineral. The pressures after successive heatings were as follows: 0.0028; 0.0061; 0.0077; 0.0110; 0.270 mm. A phosphorescent discharge was possible to some extent at this stage. On raising the pressure to 0.0298 the green helium line was permanent though not very strong. Continuing the heating, at pressure 0.0434 mm. the helium green line was permanent; the yellow fairly plain, but occasionally absent; and the violet occasionally flashed up. The discharge was entirely green and glass phosphorescent.

At pressure 0.0490, the green line was bright, the yellow line fairly bright and permanent, the violet line and also the blue line fairly good.

At pressure 0.0610, all the helium lines were easily visible; the glass still phosphorescent.

In the next experiment the tube with outside electrodes was replaced by an ordinary tube with aluminium electrodes (fig. 8). The preliminary exhaustion of the apparatus was carried to 0.00923 mm. After the 10 gm.

charcoal bulbs had been cooled the pressure fell to 0.00083 mm. The mineral was then heated with results as follows:

At pressure 0.00266, no discharge would pass.

At 0.0198 mm. pressure, the helium green, and perhaps the yellow, line was seen, as well as the green and double orange lines of mercury: all the lines faint, and the discharge in the tube weak. The spark gap in the parallel circuit was 2.5 cm.

At 0.0458 mm. pressure, the red, yellow, green and violet lines of helium were seen, also the double orange, green and blue lines of mercury. The sparking tube was then heated to expel hydrogen from the poles. After cooling it, the red, yellow, green, blue and violet lines of helium were alone visible: no mercury or hydrogen lines. The discharge passed with rather more difficulty, and the tube was phosphorescent throughout its whole length, the spark gap in the parallel circuit being $2\frac{1}{4}$ cm.

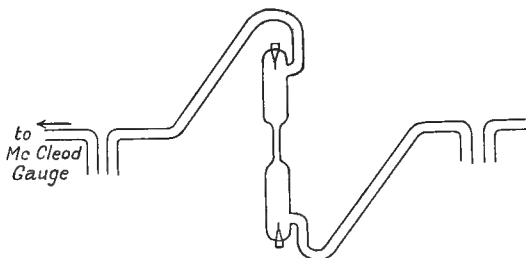


FIG. 8.

At 0.0704 mm. pressure, all the helium lines were strong. Phosphorescence appeared about the negative pole and in a ring round the base of the positive pole where the cathode stream after projection through the capillary struck the glass. The green helium line was the strongest; the colour of the discharge about the positive pole bluish green.

The spark gap required to make the resistance of the external parallel circuit exceed that of the tube was nearly 2 cm. one way of the discharge, and 1.7 cm. the other way.

At 0.0924 mm. pressure and spark gap 1.4 cm., only very slight phosphorescence appeared about the positive pole; and that about the negative pole was less than before, but still pronounced. The helium spectrum only was seen, and the green line strongest.

At 0.1447 mm. pressure and spark gap 1 cm., the phosphorescence was greatly reduced, though still distinct. The helium spectrum only, including the second violet line $\lambda 3964$ (or $\lambda 3888$?), was seen.

The marked prominence of the green ray of helium, $\lambda 5015.7$, at all the different pressures observed in these experiments is of interest in view of

Runge's theory that helium is a mixture of two gases. The green ray belongs to par-helium, which in Runge's experiments passed more quickly than helium through plaster of Paris, and may have escaped from the charcoal more readily. It was noticed in one of the previous experiments (p. 547, l. 19) that when the other rays of helium had disappeared the yellow ray still shewed at the negative pole; and also (p. 547, l. 4 from bottom) that the green ray was bright about the positive pole where the yellow ray was not seen. This looks as if the par-helium gave the kations and the helium the anions. And the increased resistance in the tube when the discharge is continued in one direction seems to indicate a polarisation of the electrodes by the absorbed gases.

Spectroscopic examination of gases expelled by heat from charcoal which had been exhausted while cold.

Two grams of charcoal were used which had been treated at a red heat with chlorine, and roasted with concentrated sulphuric acid, but not heated in an electric furnace. The large bulb of charcoal used to exhaust the apparatus after the mercury pump had been sealed off was the same as in the last described experiments. For sparking tube, that with outside electrodes was used, sealed between a small bulb containing the 2 grms. of charcoal from which the gases were extracted, and the large bulb, as in fig. 9.

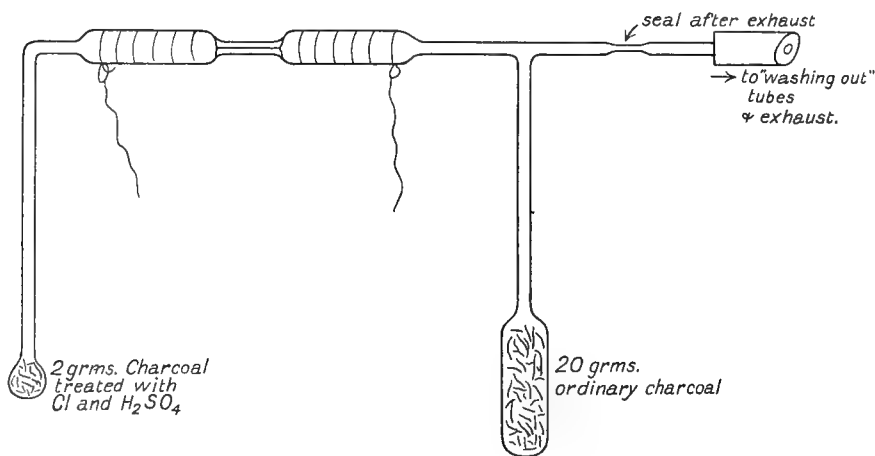


FIG. 9.

The apparatus was washed out ten times with gases from liquid air after three hours' exhaustion by the mechanical pump while the large charcoal bulb was hot. It was then sealed off the pump, and the large bulb cooled in liquid air. The electric discharge, with a spark gap of one inch in the external parallel circuit, then gave only a flashy phosphorescent discharge in the tube. The small charcoal bulb was then heated, and a lilac coloured

discharge appeared in about one minute. During a quarter of an hour's heating the following lines were observed and their readings taken with a single prism Kruss spectroscope. Their wave-lengths deduced from these readings, and the probable origin of each, are as follows:

λ	
6192	H 2nd 6196
6126	Ar 6128 or Ne 6128
5934	H 2nd 5935
5789	Hg
5768	Hg
5704	N bd 5704
5608	N bd 5612 or CO 5610
5461	Hg
5197	CO 5197
5091 to 5072	CO 5091 + N bd 5066
4920	He 4922
4833	CO 4833
4708	H 2nd 4718
4513	Ar 4511 or Ne 4513 or He 4513
4358	Hg
4349	H 2nd 4342 or Ar 4345

After half an hour's heating of the small bulb the light of the discharge in the tube was reduced to phosphorescence, no lines being visible in the spectrum.

After cooling all night the small bulb was again heated. In about five minutes some of the carbon oxide bands were feebly visible, but soon disappeared, and on continued heating the resistance of the tube steadily increased until, in about half an hour, the discharge was mainly across the gap with only phosphorescent flashes in the tube.

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